STUDIES ON HIGH RATE ANAEROBIC DIGESTION AND SUCCEEDING POLISHING UNITS

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by

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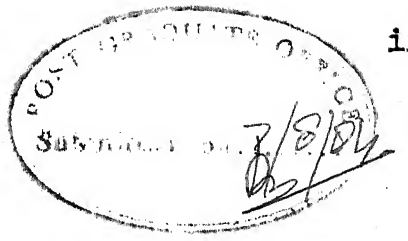

CERTIFICATE

Certified that the work presented in this thesis entitled 'Studies on High Rate Anaerobic Digestion and Succeeding Polishing Units' by Shri Bhuwan Mohan Prasad has been carried out under my supervision and it has not been submitted elsewhere for a degree.

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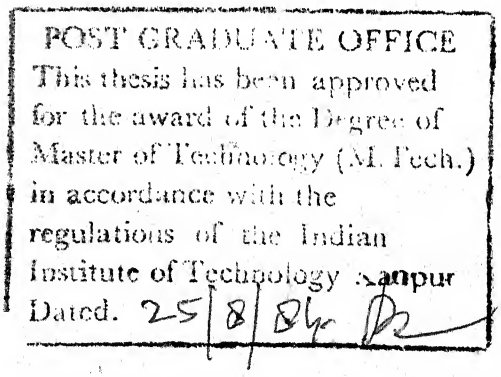

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TABLE OF CONTENTS

LIST OF TABLES	vi
LIST OF FIGURES	vii
NOMENCLATURE	viii
ABSTRACT	ix
1. INTRODUCTION	1
2. LITERATURE REVIEW	5
2.1. Process Stability	6
2.1.1. Biochemistry and Microbiology	7
2.1.2. Steps of Reaction	7
2.1.3. Six Steps in Anaerobic Digestion	12
2.2. The Process Kinetics	17
2.3. Series Operation	24
3. NEED OF PRESENT STUDY	26
4. METHOD OF STUDY AND ANALYTICAL TECHNIQUES	27
4.1. Method of Study	27
4.1.1. Composition of Feed	27
4.1.2. Experimental Set-Up	28
4.1.3. Loading Schedules	30
4.1.3.1. The Effect of Substrate Overloading in Performance of the Digester	30
4.1.3.2. Polishing Units	32
4.1.3.3. Effect of Wall Growth	33
4.1.3.4. Treatability Study of Distillery Wastes	34
4.2. Analytical Techniques	35
5. RESULTS AND DISCUSSION	37
5.1. The Effect of Substrate Overloading on the Performance of the Digester	37
5.1.1. Evaluation of Kinetic Parameters	37
5.1.1.1. μ_m and K_s Determination	38
5.1.1.2. Y and K_d Determination	38
5.1.1.3. Biomass (M) Determination	40
5.1.1.4. B_o, μ_m and K_H Determination	40
5.1.2. Comparison of the Kinetic Parameters	42
5.1.3. Performance of Digesters Under Least and the Most Stressed Conditions	48
5.1.4. Kinetics of Gas Production	50
5.2. Performance of Polishing Units Receiving Effluents from Roughing Units	53
5.2.1. Comparison of Different Digesters	53
5.2.2. Kinetic Constants for Polishing Units	59
5.3. The Effect of Wall Growth on the Performance of the Digester	63
5.3.1. Calculation of BSRT (θ_c)	63
5.4. Treatability of Distillery Waste by Anaerobic Digestion	..

6. SUMMARY AND CONCLUSIONS 66
7. ENGINEERING SIGNIFICANCE 68
8. SUGGESTION FOR FUTURE INVESTIGATION 69
REFERENCES 70
APPENDIX I 73
APPENDIX II 76
APPENDIX III 77
APPENDIX IV 78
APPENDIX V 79

LIST OF TABLES

2.1	Summary of Reactors in Series Treating Acid Whey	25
4.1	Synthetic Media Composition	30
4.2	Average Characteristics of Feed	31
4.3	Analytical Techniques	36
5.1	Evaluated Kinetic Parameters for the Anaerobic System Fed with Molasses	45
5.2	Evaluated Kinetic Constants for the Polishing Units	59
5.3	Treatability Study of Distillery Waste with S_o = 20 g/l as COD, θ = 8 days	65

LIST OF FIGURES

2.1	Reactions Performed by Acid Producing Bacteria	9
2.2	Reactions Performed by Methanogenic Bacteria	11
2.3	Conversion Processes in Anaerobic Digestion	13
2.4	Composition of digestion gas depending on the Mean Oxidation State of Carbon	15
4.1	Experimental Set-Up	29
5.1	Steady State Effluent VFA Function of Biological Solids Retention Time (BSRT). Molasses as Substrate	39
5.2	Methane Yield (B) as a Function of Biological Retention Time (θ_c)	41
5.3	Linearised Kinetic Model Relating Ultimate Methane Yield (B_o), Methane Yield (B) and BSRT (θ_c)	43
5.4	Effect of BSRT (θ_c) on Volumetric Methane Production Rate (G_s) for Different Molasses Concn. (S_o)	44
5.5	Digester Performance w.r.t. Loading Rate Molasses as Substrate	49
5.6	Kinetics of Fermentation Process at Steady State. Molasses Concn. 25 g/l as COD	51
5.7	Performance of Polishing Units for Receiving Effects from Roughing Glucose Digester (S_o = 12 g/l as Glucose, θ = 2.6 Days	55
5.8	Performance of Polishing Units for Receiving Effluents from Roughing Glucose Digester (S_o = 20 g/l as Glucose, θ = 2.6 Days)	56
5.9	Performance of Polishing Units for Receiving Effluents from Roughing Molasses Digester (S_o = 14 g/l as COD, θ = 4 Days)	57
5.10	Effect of HRT (θ) on BSRT (θ_c) for Digesters with Wall Growth	61
5.11	Performance of Digesters with Wall Growth	62

NOMENCLATURE

μ	Specific growth rate of biomass, time^{-1}
μ_m	Maximum specific growth rate, time^{-1}
S	Steady state effluent substrate concentration, mass volume^{-1}
K_s	Saturation constant, mass volume^{-1}
k	Maximum specific substrate utilisation rate, time^{-1}
x	Active biomass concentration, mass volume^{-1}
q	Specific substrate utilisation rate, time^{-1}
Y	Growth yield
K_d	Microorganism decay coefficient, time^{-1}
θ^m	The minimum biological solids retention time
S_o	Influent waste concentration, mass volume^{-1}
T_d	Microbial doubling time
V	The volume of the reactor, volume
Q	The rate of raw wastewater flowing to the tank, volume time^{-1}
B	Methane yield, volume CH_4 mass^{-1} COD added
G_s	Volumetric methane yield, volume CH_4 volume^{-1} fermenter time^{-1}
B_o	Ultimate methane yield, volume CH_4 mass^{-1} COD added
K_H	Kinetic parameter
G_{max}	Maximum volumetric methane production rate, volume CH_4 volume^{-1} fermenter time^{-1}
θ_{Gmax}	The detention time at which maximum volumetric methane production rate will occur, time
θ	Hydraulic retention time (HRT)
θ_c	Biological solids retention time (BSRT)

ABSTRACT

The present investigation was directed to evaluate kinetic constants of digesters under extremely high loading condition and performance of these digesters in terms of methane production and volatile fatty acid accumulation. The μ_m value was nearly constant (equal to 0.8 day^{-1}) for initial load while a slight decrease was noted for 56 g/l indicating inhibition of methanogenes due to overloading. There is an increase in methane production upto 40 g/l of molasses load and beyond which it decreased. The μ_m values computed from gas data were more consistant. The engineering performance of polishing units receiving effluent from roughing digester which was producing near maximum gas was probed. The polishing units provided almost 90% COD removal. The effect of wall growth on the performance of the digesters receiving molasses was studied. It was observed that even at a high loading not much inhibition took place. The wall growth contributed in terms of accumulation of microbes on the wall and thereby increasing the BSRT. The digesters with wall growth appeared to be similar to fixed film reactors in their performance. The distillery wastes were highly amicable for anaerobic digestion after its initial pH adjustment. The supplementation of nutrients was not required. Digester receiving lime treated distillery waste exhibited inferior performance than that with sodium bicarbonate treated distillery waste.

1. INTRODUCTION

The stupendous developments in modern science and technology have resulted in great exploitation of natural resources and corruption of our environment which has affected the water and the air the most the vitals of our life. It is unlikely in the near future, however, desirable it may be, that the course of exploitation and consumption be thwarted or altered. Therefore, the only other course open to us is to purify our environs and refrain from throwing away the hazardous wastes without proper treatment. However, no amount of sermonizing have been helpful. Even stringent government laws have not been able to deter the industries from discharging the effluent into the open land or into the water-ways.

Perhaps, the industrialists can only be convinced and will be tempted to treat the wastes if the treatment is made cost effective. There is a need to convince them that their wastes are not 'unwanted residue' of the industry but in fact, they are the 'resources out of place' which when treated can be a source of revenue, apart from reducing the pollution. In this regard, anaerobic treatment process seems to meet the requirements especially for high BOD wastes.

Approximately 11 x 10^6 kJ equivalent of methane is produced synthesising excess biomass of only 10 to 50 kg. of dry mass per ton COD destroyed by anaerobic processes. In contrast,aerobic processes consume approximately 8 x 10^6 kJ per ton of COD destroyed and synthesize approximately 500 kg of excess biomass (Chou et al., 1978).

Interestingly, in the same 'family' of waste - the more 'polluted' the waste is, better is the treatability. For example, glucose - the first stage waste (if at all we call it a waste!) needs the presence of all the nutrients for its bacterial decomposition; molasses-the second stage waste needs supplimentation of only some of the nutrients and lastly, the distillery waste requires least suplimentation of nutrients for efficient digestion.

Hence, for high BOD wastes which are biodegradable the choice of treatment should focus on anaerobic digestion because of the large amount of energy produced in the form of methane. In order to run the digesters to their fullest capacity with maximum efficiency and in order to avoid the digesters from getting stuck, it is essential not only to study the behaviour of microbial mass in its normal loading but also its behaviour during stressed conditions of high loadings when inhibition takes place, so that,as and when

the amount of effluents increases one may judiciously increase the loadings taking the inhibition into account. Also, with the passage of time a thick microbial coatings deposit on the digester wall which, in turn, is helpful for digestion. This enhances the biological solids retention time (BSRT) so that hydraulic retention time (HRT) and consequently volume of the reactor can be decreased or loading rate can be increased without affecting the efficiency. Further, as the detention time decreases, the rate of methane production increases, however the COD removal rate decreases. Hence, a roughing digester having very low detention time can be used to tap the methane at higher rate. A polishing unit, possibly again an anaerobic digester or an anaerobic logoon may be employed in series for maximizing COD removal rate.

The present investigation is directed to evaluate kinetic constants of digesters under extremely high loading condition and study the performance of these digesters in terms of methane production and volatile fatty acid accumulation. The engineering performance of polishing units receiving effluents from a roughing digester which is producing maximum gas, is also probed in terms of COD removal and

methane production. The effect of wall growth on the performance of the digesters receiving molasses as wastewater is studied. Initial treatability studies of distillery wastes by anaerobic digestion is also a part of this investigation.

2. LITERATURE REVIEW

Although anaerobic digestion process have been well understood in recent years, the phenomenon is as old as the civilization itself. The presence of natural gas which is nothing but methane which burned perpetually has been mentioned in myths and legends. The first person to attribute a scientific tint to this fairy-tale was Alessandro Volta. On November 17, 1976 Volta wrote a letter to a friend describing his unexpected discovery that 'combustible air' was being formed continuously and in substantial quantity in all the lakes, ponds and streams in the vicinity of Como in Italy. He associated this combustible gas with decaying vegetation. Volta's quest to characterize the inflamable gas had to be postponed, until William Henery in 1806 showed that it was apparently identical with the main constituent of a synthetic illuminating gas, which was later called methane (Sathanathan 1979). However, it took another century, since Volta, until methanogenesis was found to be connected with microbial activity. The knowledge of the biology, physiology and biochemistry of methane bacteria has developed slowly over a long period of time, but still many aspects are yet to be explored. Despite all these, anaerobic treatment processes are being considered today as one of the possible means to recover

energy in the form of methane and at the same time, reduce the pollutional load of organic wastes. Various anaerobic process configuration have found widespread usage in the treatment of municipal sludges and more recently, in the treatment of organic industry wastes like, sugar and distillery industry wastes, tannery wastes, slaughter - house wastes, and animal manure slurries, (Chen et al. 1980, Brown et al. 1982,Landine et al. 1982, Grasius, 1983).

Pfeffer et al.(1967) reports that the major advantage of anaerobic treatment are (1) less biomass produced per unit of substrate (organic material) utilized, which also means a decrease in the requirement for nitrogen and phosphorus; (2) economic value of the methane gas generated in the treatment process. and (3) higher organic loading potential because the process is not limited by oxygen trasfer capability at high oxygen utilization rates. In order to extract the above attractive advantages optimally, it is essential to understand the biochemistry and microbiology of microbes, besides the engineering aspects of the system.

2.1 Process Stability

In the anaerobic digestion process, the organic material in the waste is biologically converted to methane and carbon dioxide in the absence of molecular oxygen. This

process is mediated by different groups of facultative and obligate anaerobic microbes.

2.1.1 Biochemistry and Microbiology:

The biochemistry and microbiology of anaerobic process is much more complicated than that of aerobic ones because of many pathways available for the anaerobic community. The pathways and micro-organisms responsible for the reactions are not known in great details, but during the last 10-15 years a broad outline of the processes has been established as described by a number of investigators (McCarty 1964, Lawrence and McCarty 1969, Toerien 1969, Baleh et al. 1979, Zikas 1977).

Basically the anaerobic degradation, performed by two groups of bacteria are the acid producing and the mathane forming types. These two groups can be sub-divided into two groups each. Acid producing bacteria as (i) Acid forming bacteria (butyric and propionic acid) and (ii) Acetogenic bacteria (acetic acid and hydrogen). Methane producing bacteria as (i) Acetoclastic methane bacteria (acetophilic) and (ii) Methane bacteria (hydrogenophilic).

2.1.2 Steps of reaction

The anaerobic metabolism of a complex substrate, including suspended organic matter, can be regarded as a three step process:

1. Step: Hydrolysis of suspended organics and soluble organisors of high molecular weight.

2. Step: Degradation of small organic molecule to various fatty acids, ultimately acetic acid.

3. Step: Production of methane, primarily from acetic acid but also from hydrogen and carbon dioxide.

Hydrolysis of organic matter is rather slow process brought about by extracellular enzymes and to same degree the pH of the liquid. Lipids are hydrolyzed very slowly, with the result that the hydrolysis step may be overall (including methane production) rate limiting for wastes containing considerable amount of lipids, and other slowly hydrolyzing compounds.

The type of lipid apparently plays a role, as the degradation of nonpolar lipids in anaerobic processes seem to be considerably slower than the degradation of polar substances (Termofil 1981).

Eastman and Ferguson (1981) have demostrated that in a separate acid producing reactor, the hydrolysis is always the rate limiting step. Acid production results in formation of acetic acid or in case of instability, the higher fatty acids such as propionic, butyric, isobutyric, valeric and iso-voleric acid. A general outline of the metabolic pathways of the acid producing bacteria is presented in Fig. 2.1.

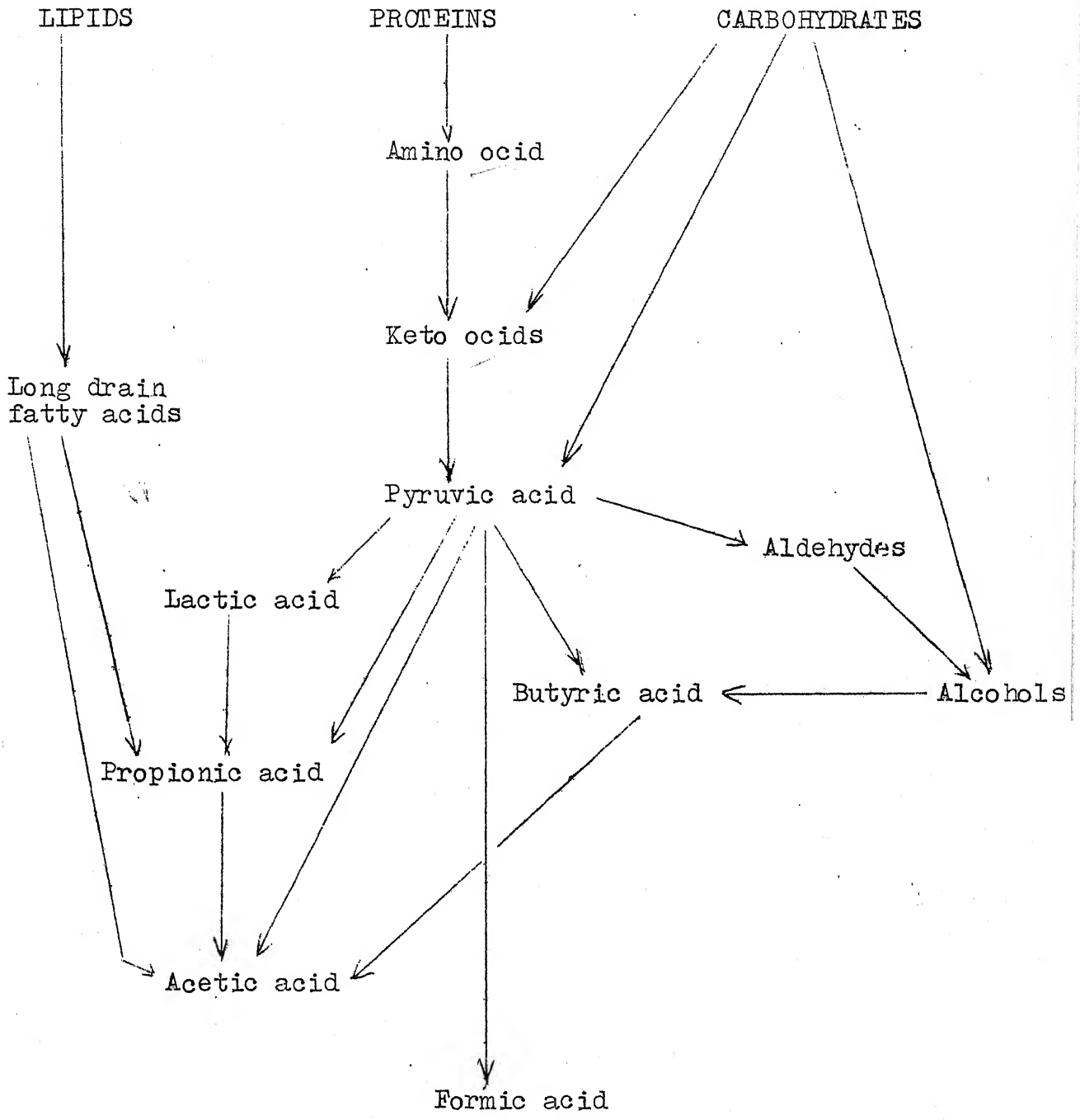


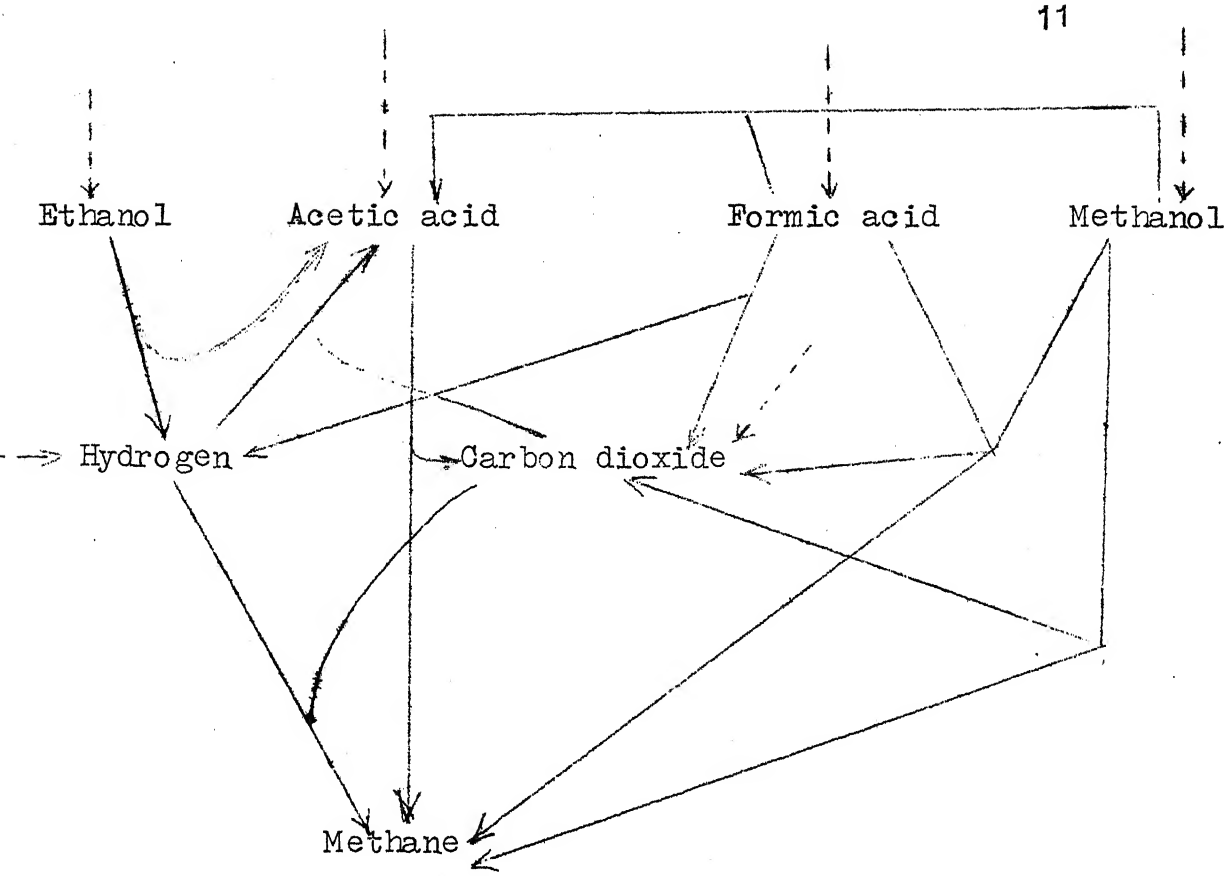
Fig. 2.1 Reactions performed by acid producing bacteria. Only major routes indicated (based on STAFFORD (1980), SIXT (1979), MOSEY (1982) and others).

(Adopted from Henze and Harremoes, 1982)

In a stable anaerobic process the concentration of fatty acid is fairly low (100-300 mg/l). Increased concentration are indication of load variation or a process operating near its maximum (with a minimum safety factor). During upstart of anaerobic process the volatile acid concentration should be kept reasonably low (< 500 -1000 mg/l). Mosley (1982) postulated in his models for short-chain volatile acids, that hydrogen partial pressure (or redox potential) regulates the production of the various acids. For digesters operating at very short detention time the concentration of propionic acid and hydrogen is increased.

The acid production rate is high as compared to the methane production rate, which means that a sudden increase in easily degradable (soluble) organics will result in increased acid production with subsequent accumulation of the acids. This might inhibit the next step of the process, the methane step. Parallel to the acid production, ammonia is released by the degradation of proteins and amino acids (McCarty, 1978). The ammonia-concentration, thus established will generally not be of a magnitude that will inhibit the anaerobic process but for nitrogen rich wastes treated in highly loaded processes, ammonia inhibition could occur.

Methane production is a slow process, in general the rate-limiting step of the anaerobic degradation. Methane is



- - - - -> External production (from outside this figure)

Fig. 2.2 Reactions performed by methanogenic bacteria (based on SIXT (1979), STAFFORD (1980), ZEHNDER (1978), MOSEY (1982 and others).
(Adopted from Henze and Harremoes, 1982)

produced from acetic acid on from hydrogen and carbon dioxide. About one third of the methane has its origin in molecular hydrogen (Jeris McCarty 1965). Small amounts of methane can be produced from methanol (Smith and Moh 1978) and formic acid but then reactions have little practical important Fig. 2.2 depicts the main processes performed by the methane producing bacteria.

The bacteria producing methane from hydrogen and carbon dioxide are fast growing ones as compared with the acetic acid utilizing bacteria. The latter are in every respect the primadomes of anaerobic digestion. When conditions are so, that they protiferate, all other bacteria species necessary for the anaerobic degradation will also thrive. This does not necessary mean that the methane producing reaction is rate limiting, the hydrolysis may have that role (Gujer and Zehnder, 1982). The difference between the two is that the methane bacteria must exist in the reactor, while the hydrolysis of degradable suspended solids might be beneficial for the process but not essential for the process of function.

2.1.3 Six Steps in Anaerobic Digestion:

In 1977 Kaspar had identified six different conversion processes which was modified by Gujer and Zehnder (1984) and is shown in Fig. 2.3.

Conversion processes in anaerobic digestion

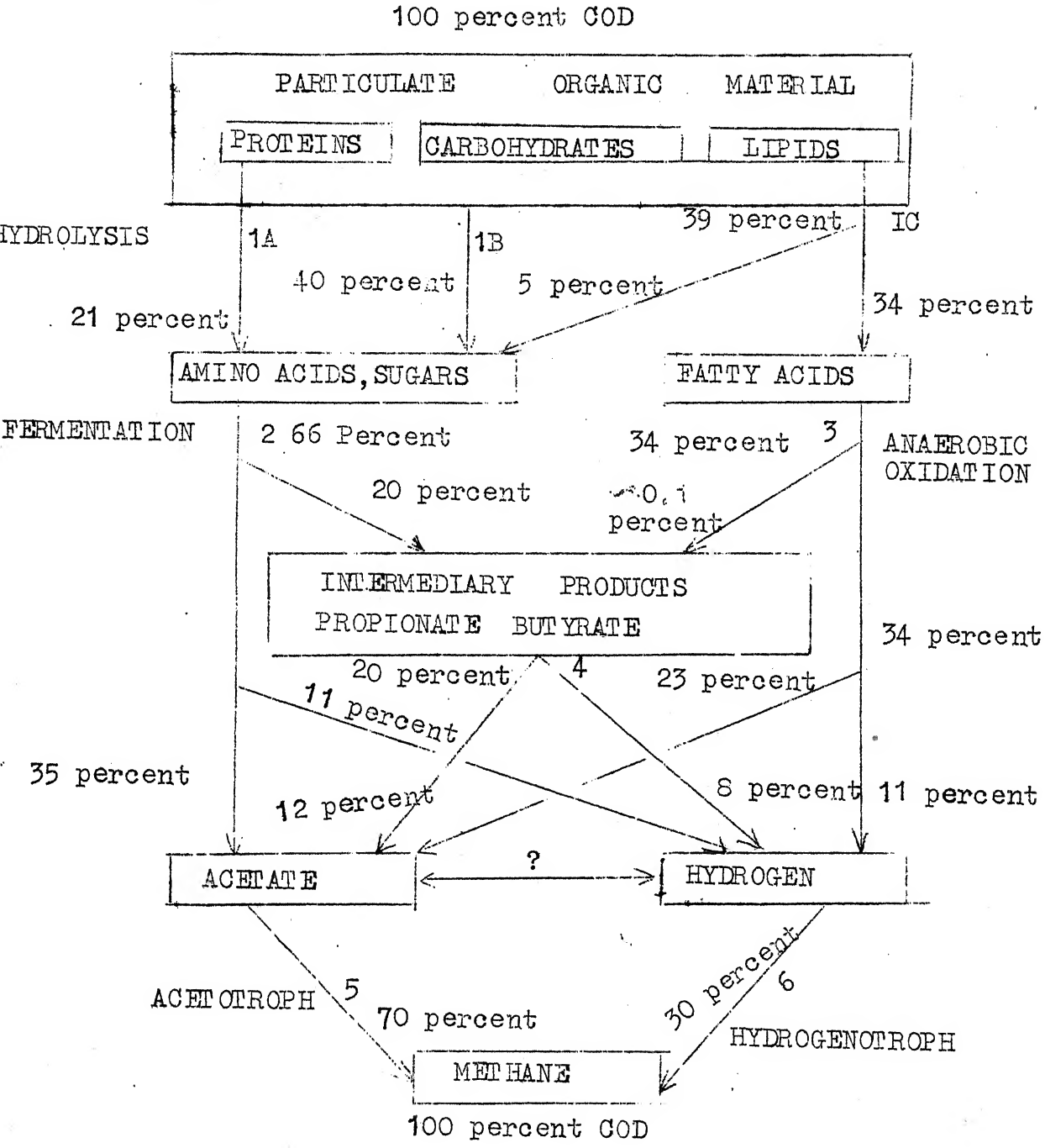


Fig. 2.3 Proposed reaction scheme for the anaerobic digestion of domestic sludge.

Adapted from Gujer and Zehnder (1983)

Six distinct processes may be identified in the anaerobic digestor:

1. Hydrolysis of bioploymers
   1A Hydrolysis of protein
   1B Hydrolysis of carbohydrates
   1C Hydrolysis of lipids
2. Fermentation of amino acids and sugars
3. Anaerobic oxidation of long chain fatty acids and alcohols
4. Anaerobic oxidation of intermediary products such as volatic acid (with the exception of acetate).
5. Conversion of acetate to methane
6. Conversion of hydrogen to methane.

The fluxes in Fig. 2.4 are expressed as COD. Digester gas contains predominently methane and carbon dioxide. If the carbon (and not sulfur or nitrogen) prevails as a sink of electron (or hydrogen), the production of methane is a consequence of the COD reduction. A prediction of CO_2 gas formation is more complex since CO_2 remains dissolved in the digester liquor or is converted to bicarbonate as a function of amonia concentration. Thus, the composition of the digester

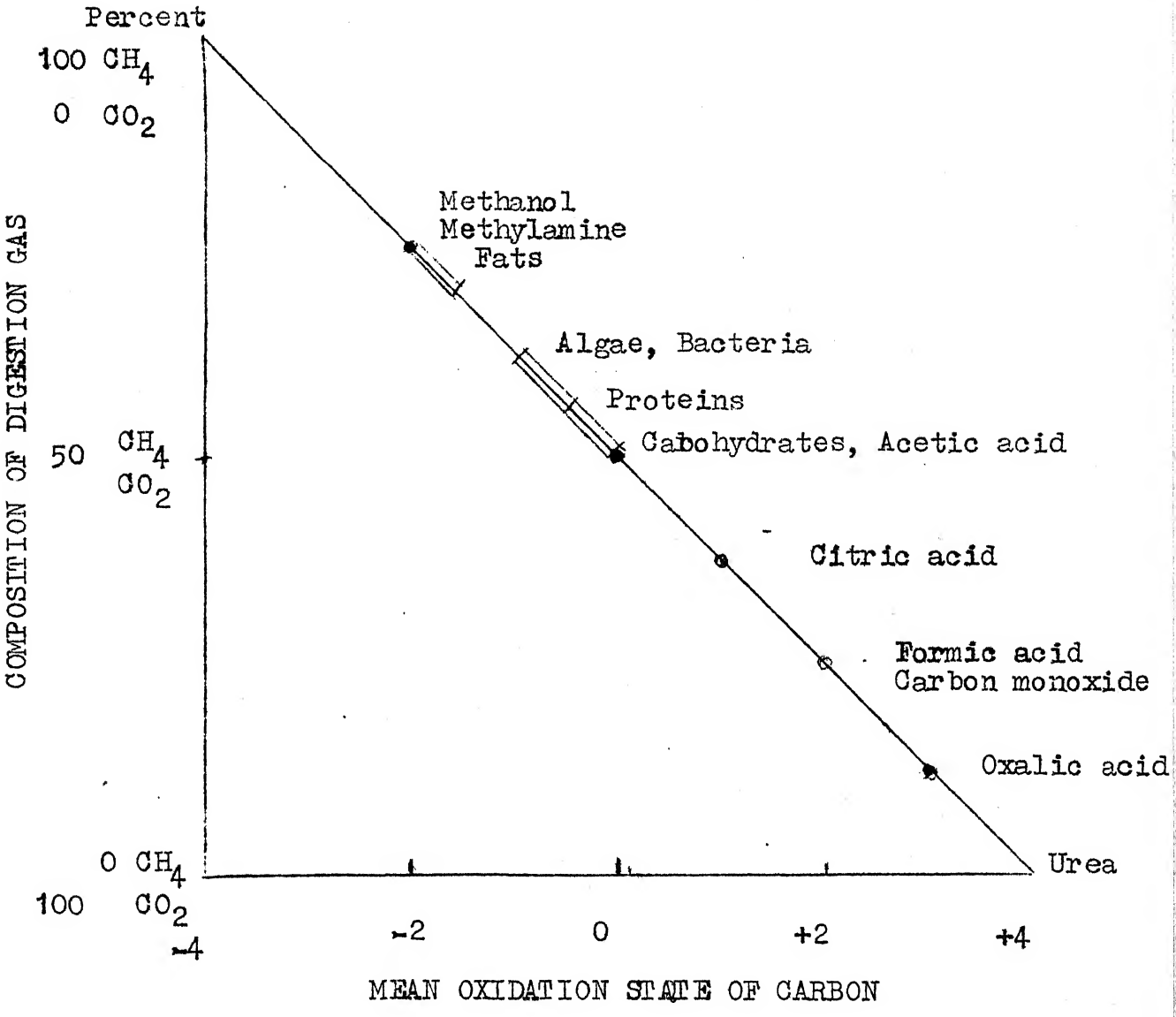


Fig. 2.4 Composition of the digestion gas depending on the mean oxidation state of the carbon in the substrate, assuming total mineralisation of the substrate. Adapted from Gujer and Zehnder (1983).

gas depends mainly on the mean oxidation state of the carbon in the organic matter (Fig. 2.4) as well as the CO_2 saturation of the digestor liquor and the nitrogen content of the organic material degraded (ammonia is released during decomposition of of nitrogenous compounds). The mean oxidation state of the sludge can be calculated from the following relation:

$$\bar{OS} = 1.5 \frac{COD}{TOC} - 4$$

$\bar{OS}$ = mean oxidation state of the carbon degraded

COD = amount of COD degraded (Mass unit)

TOC = amount of organic carbon degraded (Mass unit).

If the composition of the substrate is known and the entire sub-strate is converted to gas, the theoretical methane yield can be calculated from the following equation (symons and Buswell, 1933):

$$C_n H_a O_b + (n - \frac{a}{4} - \frac{b}{2}) H_2O \rightarrow (\frac{n}{2} + \frac{a}{8} - \frac{b}{4}) CH_4 + (\frac{n}{2} - \frac{a}{8} + \frac{b}{4}) CO_2$$

2.2 The Process Kinetics

All biological wastewater treatment processes take place is a volume defined by a specific boundaries. Such a volume is commonly termed as recter. Changes in the composit and concentration of materials that occur while the wastewate is retained in the reacter are important factors in wastewate treatment. These changes are caused by hydraulic transport o materials into and out of reacter as well as by reactions tha occur within the reactor. To fully define a reacter system a design similar ones, it is necessary to know the rate at which the changes occur and the extent of the changes (Benefield and Randall, 1980).

As mentioned earlier, from the kinetic viewpoint, anaerobic treatment may be broadly divided into three step processes involving (a) hydrolysis of complex material, (b) acid production and (c) methane fermentation. In such a multistep process, the slowest step will govern the overall kinetics of waste stabilization. The slowest or rate limiti step anaerobic treatment is the third-step, that is methane fermentation (Lawrence et al.,1969; Cohen et al.,1979; Benefield and Randall, 1980).

The relationship between the residual concentration the growth-limiting nutrient and the bacterial growth rate is given by Manod (1949) as follows:

$$\mu = \mu_m \frac{S}{K_s + S} \qquad (2.1)$$

where

μ = specific growth rate of biomass, $time^{-1}$, which can defined as $\frac{(dx/dt)}{x}$, where x is the concentration of biomass present.

μ_m = maximum value of μ at saturation concentration of growth-limiting substrate, $time^{-1}$

S = residual growth-limiting substrate concentration, mass $volume^{-1}$

K_s = saturation constant numerically equal to the substrate concentration at which $\mu = \mu_m/2$, mass $volume^{-1}$.

Lawrence and McCarty (1969) have related the rate of substrate utilization to the concentration of micro-organism in the digester and to the concentration of substrate surrounding the organism by the equation

$$\frac{ds}{dt} = \frac{kx\,S}{K_s + S} \qquad (2.2)$$

where

(ds/dt) = overall substrate utilization rate, mass $volume^{-1}$ $time^{-1}$

K = maximum specific substrate utilization rate, $time^{-1}$

S = Substrate concentration surrounding the biomass, mass $volume^{-1}$

K_s = saturation constant, which has a value equal to the substrate concentration when $(ds/dt)/x = k/2$, mass volume^{-1}

x = active biomass concentration, mass volume^{-1}

Equation 2.2 can also be written as

$$q = \frac{k\,S}{K_s + S} \qquad (2.3)$$

where

q = specific substrate utilization rate, time^{-1}, which is defined as $(ds/dt)/x$

Growth yield, Y, is defined as

$$Y = (dx/ds) \qquad (2.4)$$

which can also be written as

$$\frac{dx}{ds} = \frac{(dx/dt)/x}{(ds/dt)/x}$$

Therefore,

$$Y = \frac{\mu}{q} \qquad (2.5)$$

However, in bacterial systems, not all energy goes for the growth of the cell. A part of this energy goes for the maintenance of the cell known as endogenous respiration and the endogenous decay term must be incorporated in the above equation (McCarty, 1969). Hence, the above equation will reduce to:

$$= Yq - K_d \qquad (2.6)$$

where

K_d = microorganism decay coefficient, time^{-1}.

A term that is closely related to specific utilization rate (q) that is commonly used in practice is known as food-micro-organism ratio (F/M) and hence equation (2.5) can also be written as (Metcalf and Eddy, 1975):

$$\mu = Y\left(\frac{F}{M}\right) - K_d \qquad (2.7)$$

Andrew (1969) incorporated yet another term in the equation 2.1 taking into account the inhibition factor due to overloading. The modified equation by him is as follows:

$$\mu = \frac{\mu_m}{1 + \frac{K_s}{S} + \frac{S}{K_I}} \qquad (2.8)$$

where,

K_I = inhibition constant, numerically equal to the highest substrate concentration at which the specific growth rate is equal to 1/2 the maximum specific growth rate in the absence of inhibition, mass volume^{-1}.

Lawrence and McCarty (1970) introduced an operational parameter called biological solids retention time (BSRT)

symbolized by θ_c which is defined as the average time a unit of biomass remains in the treatment system.

Considering the material balance equation for biomass in a reactor, it can be obtained as

$$\mu = \frac{1}{\theta_c} \qquad (2.9)$$

and also $\mu_m = \frac{1}{\theta_c^m}$ (2.10)

where

θ_c^m = the minimum biological solids retention time the BSRT at which biomass is removed from the systems faster that it is being produced.

For a reactor without biomass recycle, BSRT (θ_c) and hydraulic retention time (HRT -θ) are same.

Process failure due to kinetic stress will occur when the BSRT (θ_c) is reduced to θ_c^m. Under this condition waste treatment efficiency drop to zero and the effluent waste concentration, S, is equal to the influent waste concentratio S_o. When S_o is large enough to be non-growth-limiting, the value of θ_c at which process failure occurs is a characteristic of the waste as well as waste assimilating microbial population. In such case, $S_o = K_s + S_o$ and thus equation 2.3 changes to $q = \frac{k}{K_s} = k'$ and hence equation 2.6 changes to

$$\mu_m = \frac{1}{\theta_c^m} = Yk' - K_d \qquad (2.11)$$

Again, $1/\theta_c^m$, the maximum specific growth rate of the process micro-organism is related to the 'doubling' or generation time, used to charactrize bacterial species as

$$T_d = \frac{.69}{\mu_m} \qquad (2.12)$$

where,

T_d = time required to double the microbial mass at high non-growth-limiting substrate concentration, time.

Chen et al. (1978) have taken entirely a different approach to explain the process kinetics of biomethanation. They refer to the final product of digestion process, i.e. the methane gas and, a kinetic model discribing the methane fermentation rate as a function of waste bio-degradability, loading rate, and detention time for a continuous, continuously mixed fermentation system without solids recycle was proposed:

$$B = B_o \left(1 - \frac{K_H}{\mu_m \theta^{-1} + K_H}\right) \qquad (2.13)$$

or

$$G_s = \frac{B_o S_o}{\theta} \left(1 - \frac{K_H}{\mu_m \theta^{-1} + K_H}\right) \qquad (2.14)$$

where

B = methane yield, volume CH_4 volume^{-1} fermenter time^{-1}

G_s = volumetric methane yield, volume CH_4 volume^{-1} fermenter time^{-1}

B_o = ultimate methane yield, volume CH_4 mass^{-1} COD added as $\theta \rightarrow \infty$

S_o = influent total COD, mass volume^{-1}

θ = retention time, time

μ_m = maximum specific growth rate of micro-organism, time^{-1}

K_H = kinetic parameter, dimensionless.

The maximum volumetric methane production rate, G_{max}, was obtained by taking the derivative of G_s with respect to θ and equating it to zero. So,

$$G_{max} = B_o S_o \mu_m/(1 + \sqrt{K_H})^2 \qquad (2.15)$$

which occurs at a detention time, θ_{Gmax}.

$$\theta_{Gmax} = (1 + \sqrt{K_H})/\mu_m \qquad (2.16)$$

Chen et al. (1980) studied the effect of temperature on methane fermentation kinetics of Beef-Cattle Manure. In semi-continuous systems, plotting the steady-state methane yield (litre Ctta/g vs added) versus the reciprocal of BSRT θ_c and extrapolating to an infinite θ_c (i.e., as $1/\theta_c \rightarrow 0$), the ultimate methane yield (B_o) were found out. Using equation 2.13, with a non-linear least-square fit of experimental data. They found the value of μ_m and K_H.

Substituting the value of B_o, K_H and μ_m, for known value of S_o, they also calculated G_{max} and θ_{Gmax}.

Later Hashimoto (1982) studied the effect of volatile concentration (S_o) and θ on CH_4 production from cattle waste. It is reported that, the kinetic parameter K_H increases exponentially as S_o increases as follows:

$$K_H = 0.8 + 1.0016\ e^{.06S_o} \qquad (2.17)$$

This increase in K_H indicates inhibition of fermentation, according to Hashimoto (1982).

The kinetic models proposed by Chen et al. (1978) are of immense benefit, as they predict the detention time for maximum methane production. The value of B_o for a particular waste is a good measure of its biodegradability. However, these equations are incapable of predicting the degree of treatment or effluent quality. The kinetic parameter K_H is a function of the influent substrate concentration and type of substrate and hence evaluation of K_H and other parameters for different wastewaters are essential for designing a treatment system which also produces maximum gas.

2.3 Series Operation

Hickey and Owens (1981) studied the effectiveness of operating reactors in series by treating acid whey with the anaerobic biological fluidized bed. The result is reported in Table 2.1.

Table 2.1 Summary of Reactors in Series Treating Acid Whey

	Organic Loading Rate kg COD/m^3/day	COD's Influent	Mg/l Influent	Percent Removal	HRT days
Reactor 1	37.6	52260	14590	72	1.4
Reactor 2	2.7	14590	3250	78	3.6
Overall	10.5	52260	3250	94	5.0

The first reacter in the treatment train was operated as a roughing unit (loaded at 37.6 kg COD/m^3/day). The second reacter received a portion of reactor No. 1's flow and served as a polishing unit. Reacter No.1 removed 72 percent of the COD while reacter No. 2 removed 87 percent of the residual COD, for an overall COD removed was 94 percent. The combined hydraulic retention time was 5.0 day (1.4 days in reacter No. 1 and 3.6 days in reacter No.2), which was equivalent to an overall loading rate of 10.5 kg COD/m^3/day. However, only 85 percent COD removal has been achieved for one reacter at this loading.

3. NEED OF PRESENT STUDY

In order to understand the behaviour of microbial population in the anaerobic digester completely, it was felt that, besides its normal loadings, the process should also be studied in terms of kinetic constants when it is overloaded. This need was also due to the reason that - a particular industry may like to expand over a period of time and consequently, increase the effluent quantity. Going for all together new reacters may not be economical. Perhaps, if the existing digesters themselves are judiciously overloaded without affecting their performances much, the situation will be an ideal one.

The overloaded reacters normally produce volumetrically more methane than others at an optimal loading rate. However, COD removal is not to the desired extent. Hence, in order to meet these twin criteria simultaneously, it was felt to operate two digesters in series - first for producing methane at its highest rate and the subsequent one for removing COD to maximum possible extent.

Over a period of time, a thick microbial mass deposits on the inner walls of the digester which increases BSRT and thus the capacity of the digester. However, no systematic study has been documented, so far. Therefore, it was felt necessary to study the behavioural parameters on these digesters.

4. METHOD OF STUDY AND ANALYTICAL TECHNIQUES

4.1 Method of Study

In the present study, glucose as a simple substrate, molasses as industrially produced complex substrate and distillery waste as an industry waste have been used. The semi-continuous digesters operating at different substrate concentrations and different hydraulic detention times were employed.

4.1.1 Composition of feed

In all, three kinds of feed were used which are as follows:

(a) Glucose - An analytical reagent of BDH company was used. In order to supplement with required growth nutrients a synthetic media containing nitrogen, phosphorus and other trace elements as given in Table 4.1 (Krocker et al. 1979) was used. The seed for these digesters were taken from the glucose digesters already in operation in Environmental Engineering Laboratory (of whose seed were, in turn, taken from a cow-dung digester maintained at 20 days hydraulic retention time, fed with 20 percent cow-dung slurry on alternate days).

(b) Molasses was collected from National Sugar Institute, Kanpur and was diluted to obtain the required COD for loading the digesters. The average composition of molasses is given in Table 4.2. The nutrient and seed used were same as in (a).

(c) Distillery waste - Distillery waste which was basically the 'spent wash' was collected from a distillery industry. The average composition of the distillery waste is given in Table 4.2. The required growth nutrient, here, was only Nitrogen, so .04 gm of urea per g of COD of waste was used. The seed was taken from the molasses digesters, already in operation.

In all the cases, IIT Kanpur Campus tap water was used for dilutions and other purposes. Sodium bicarbonate was used for maintaining the pH within the required anaerobic pH range. Roughly for one gm of COD of glucose, molasses and distillery waste - 10 ml, 7 ml and 30 ml of 30 g/l of bicarbonate solution were needed, respectively.

4.1.2 Experimental Set-up:

An experimental set-up as shown in Fig. 4.1 was used for the study. Except for the polishing digesters where one-litre glass aspirator bottles were used, two-litres aspirator bottles were used for other digesters. The

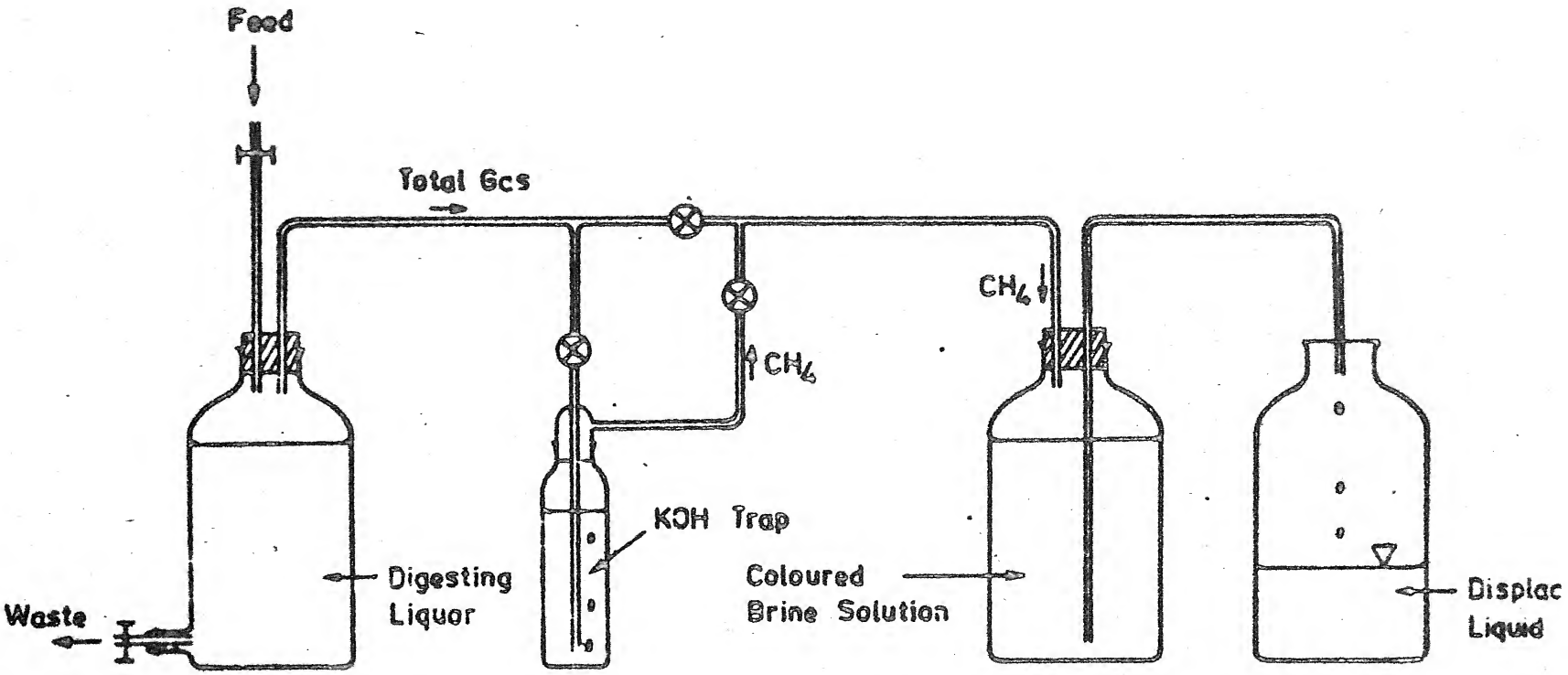


Fig. 4.1. Experimental Set-up

Table 4.1 Synthetic Media Composition* (Kroeker et al. 1979)

Compound	Concentration, mg/l
KH_2PO_4	4000
$MgSO_4\ 7H_2O$	126
$CoCl_2.6H_2O$	36
$FeCl_3.6H_2O$	864
$CaCl_2.6H_2O$	6000
Urea	4000
Yeast Extract	400

* The medium constituted one fourth of the daily feed.

digester bottles were placed in a constant temperature water bath, maintained at 37 ± 2°C. The gas production was measured using liquid displacement of saturated sodium chloride solution containing 5 percent by volume of H_2SO_4 and methyle orange.

4.1.3 Loading Schedules: The following different sets of experiments were carried out.

4.1.3.1 The effect of substrate overloading in Performance of the digester.

Using molasses as the substrate, five digesters were run with the following influent loads as mg/l of COD (S_o) and detention times (θ) combinations:

Table 4.2 Average Characteristics of Feed

Parameter	Concentration, g/l except pH	
	Molasses 100 g dissolved in 1 l of water	Distillery – 'spent wash'
pH	5.5 – 6.5	4.0 – 4.5
BOD	61	62
COD	78	89
Total Nitrogen as N	0.4	0.75
Potassium as K	2.25	7.125
Calcium as Ca	1.06	–
Total carbohydrate as glucose	43.03	17
Reducing sugar as glucose	11.6	15
Volatile solids (VS)	57.3	43
Fixed solids (FS)	6.56	18

Set (i) Influent molasses. COD = 24 g/l

Various HRTs = 8,6,4,3,2,1.6 days

Set (ii) Influent molasses, COD = 32 g/l

Various HRTs (θ) = 8,6,4,3,2 days

Set (iii) Influent molasses, COD = 40 g/l

Various HRTs (θ) = 8,6,4,3,2 days

Set (iv) Influent molasses, COD = 48 g/l

Various HRTs (θ) = 8,6,4,3,2 days

Set (v) Influent molasses, COD = 56 g/l

Various HRTs (θ) = 10,6,4,3,2 days.

4.1.3.2 Polishing units:

Following three combinations were used for this purpose.

(i) A glucose digester having S_o = 12 g/l was brought steadly from higher θ (8 days) to θ = 2.67 days and maintained at this level as roughing units. The effluents from this digester was fed to five polishing units using appropriate volumes so as to yield the different HRTs like 4,6,8,10 and 16 days.

(ii) Another glucose digester with S_o = 20 g/l as glucose was stablized at θ = 2.67 days and its effluent was fed to six polishing digesters to yield HRTs (θ) = 4,6,8,10, 16 and 20 days.

(iii) A molasses digester with S_o = 14 g/l as COD and θ = 4 days was used as roughing unit and the effluents of its was fed to three polishing units maintained at

4.1.3.3 Effect of wall growth:

One digester with glucose and two digesters with molasses as their substrate were allowed for the wall growth. These digesters were run for quite some time at lower detention times so that the micro-organism proliferate on the inner walls. The following combinations were tried:

Set (i) Glucose: Influent glucose conc. = 12 g/l as COD
Various HRTs (θ) = 2.4, 2, 1.6, 1.33, 1 days.

Set (ii) The digester with one day HRT was subjected to various influent glucose concentrations like 12, 14, 16 and 20 g/l to study the effect of cover-loading on wall growth.

Set (iii) Influent molasses, COD = 32 g/l
Various HRTs (θ) = 2.6, 2, 1.6, 1.33, 1.11, 1

Set (iv) Influent molasses COD = 40 g/l
Various HRTs (θ) = 2.0, 2, 1.6, 1.33, 1.11, 1.

Apart from the above sets, one glucose digester which was maintained at S_o = 2 g/l as glucose and θ = 8 days and had developed growth on the walls, a loading of 20 g/l of glucose with θ = 1 days, was fed to see the effect of the shock loading on the microbial wall growth.

4.1.3.4. Treatability Study of Distillery Wastes

Three digesters with distillery wastes as substrate with following combinations were used:

(a) S_o = 20 g/l as COD and θ = 8 days bicarbonate treated without nutrient

(b) S_o = 20 g/l as COD and θ = 8 days bicarbonate treated with nutrient

(c) S_o = 20 g/l as COD and θ = 8 days lime treated with nutrient.

All these digesters were operated as semi-continuous system. After thoroughly shaking the digesters, a definite quantity of mixed liquor depending upon the HRT was withdrawn everyday and immediately replacing it was replaced with the equal quantity of the required feed.

After the digesters had been maintained at the designated θ for two hydraulic turnovers to ensure steady state, three consecutive daily effluent samples were analysed for pH, volatile fatty acid (VFA), bicarborate alkalinity, inorganic phosphate and COD. Besides, monitorihg the total gas production, the methane content of the gas was assessed by passing it through a KOH trap (6 N Solution). (A few gas samples were subjected to chromolographic analysis for determination of CH_4, CO_2 and H_2).

Except for the digesters which were studied for the wall growth, care was taken to avoid similar kinds of growth in the other digesters by flushing it with nitrogen gas.

4.2 Analytical Techniques

The effluents from the digestors were taken for analysis. After measuring the pH of the effluent (the sample), the sample was centrifuged using Janetcki (Model K-24, East Germany) at 8500 xg and then the supernatent was taken for further analysis. The various analytical methods alongwith equipments and references have been given in the Table 4.3.

Table 4.3 Analytical Techniques

No.	Parameter	Equipment/Method	Reference
	pH	Systronic, Model 331, India	Standard Method (1976)
	Volatile Acid	Direct Titrametric Method with phosphate correction	(i) De Lallo et al(1961) -Titremetric Method. (ii) Tauskey and Shorr (1972) -Phosphate (iii) Grasius (1983) - Phosphate correction
	BOD	Incubation at 20°C for 5 days	Standatd Methods (1976)
	COD	Potassium dichromate, Refluxing Method	Standard Methods (1976)
	Reducing Sugar	Arsenomolybdate Method	Somogeji (1952)
	Nitrogen Total	Digestion and Nessleriation, Kjeldahl's Method	Thompson et al. (1951)
	Calcium	EDTA Titrimetric Method	Standard Methods (1976)
	Total carbohydrate	Phenol-Sulferric Acid Method	Dubois et al. (1956)
	Sulfate	Gravimetric Method	Standard Methods (1976)
	Phenol	Flame Photometer (Model CL-22A, Elico Pvt. Ltd.)	Manual of Manufacturer
	Volatile Suspended Solids (VSS)	Muffle Furnace	Standard Methods (1976)
	Gas Analysis	GLC (Model-761 MS, CIC, India)	Manual of Manufacturer

5. RESULTS AND DISCUSSION

As mentioned in the previous chapter, the entire study can be divided into four distinct sub-heads, namely,

(1) The effect of substrate overloadings on the performance of the digester and evaluation of kinetic parameters for the process design.

(2) Performance of polishing units receiving effluents from overloaded roughing units in terms of COD removal and gas production. Also, the kinetic constants for polishing units have been evaluated.

(3) The effect of wall growth on the performance of the digester.

(4) Treatability of distillery waste by anaerobic digestion.

5.1. The Effect of Substrate Overloading on the Performance of the Digester

5.1.1. Evaluation of Kinetic Parameters

The kinetic parameters for methane fermentation were evaluated employing semi-continuous digesters without sludge recycle, fed with molasses. Five digesters with influent substrate concentration (S_o) of 24, 32, 40, 48, and 56 g/l were used to study the effect of overloading. These digesters were subjected to a programme of steady state operations at various biological solids retention times (BSRT) as given in Section 4.1.3.1. The system parameters were measured after the digesters have obtained steady state at each load and detention time.

5.1.1.1. μ_m and K_s Determination

The kinetic constants μ_m and K_s were determined using the steady state VFA values for different detention times as follows.

Taking reciprocal on both sides of equation 2.1

$$\frac{1}{\mu} = \frac{K_s}{\mu_m}\left(\frac{1}{S}\right) + \frac{1}{\mu_m} \qquad 5.1$$

Considering equation 2.9, equation 5.1 can be written as

$$\theta_c = \frac{K_s}{\mu_m}\left(\frac{1}{S}\right) + \frac{1}{\mu_m} \qquad 5.2$$

A plot of θ_c versus 1/S yielded the constants μ_m and K_s. These constants for methane formers were obtained using the steady state effluents VFA. Figure 5.1 represents the plot of equation 5.2 using VFA values for S for the molasses concentration of 24, 32, 40, 48, and 56 g/l as COD. The reciprocal of μ_m gave the minimum detention time θ_c^m. These values are summarized in Table 5.1.

5.1.1.2. Y and K_d Determination

Y and K_d for the methane formers were evaluated using equation 2.6 in which μ and q are variable. q was calculated using equation 2.3

$$q = \frac{kS}{K_s + S}$$

The value of k, maximum specific substrate utilization rate, was adopted from Grasius (1983) as 10.38 day^{-1}. Substituting K_s values already estimated in the section 5.1.1.1, q was determined for various steady state VFA

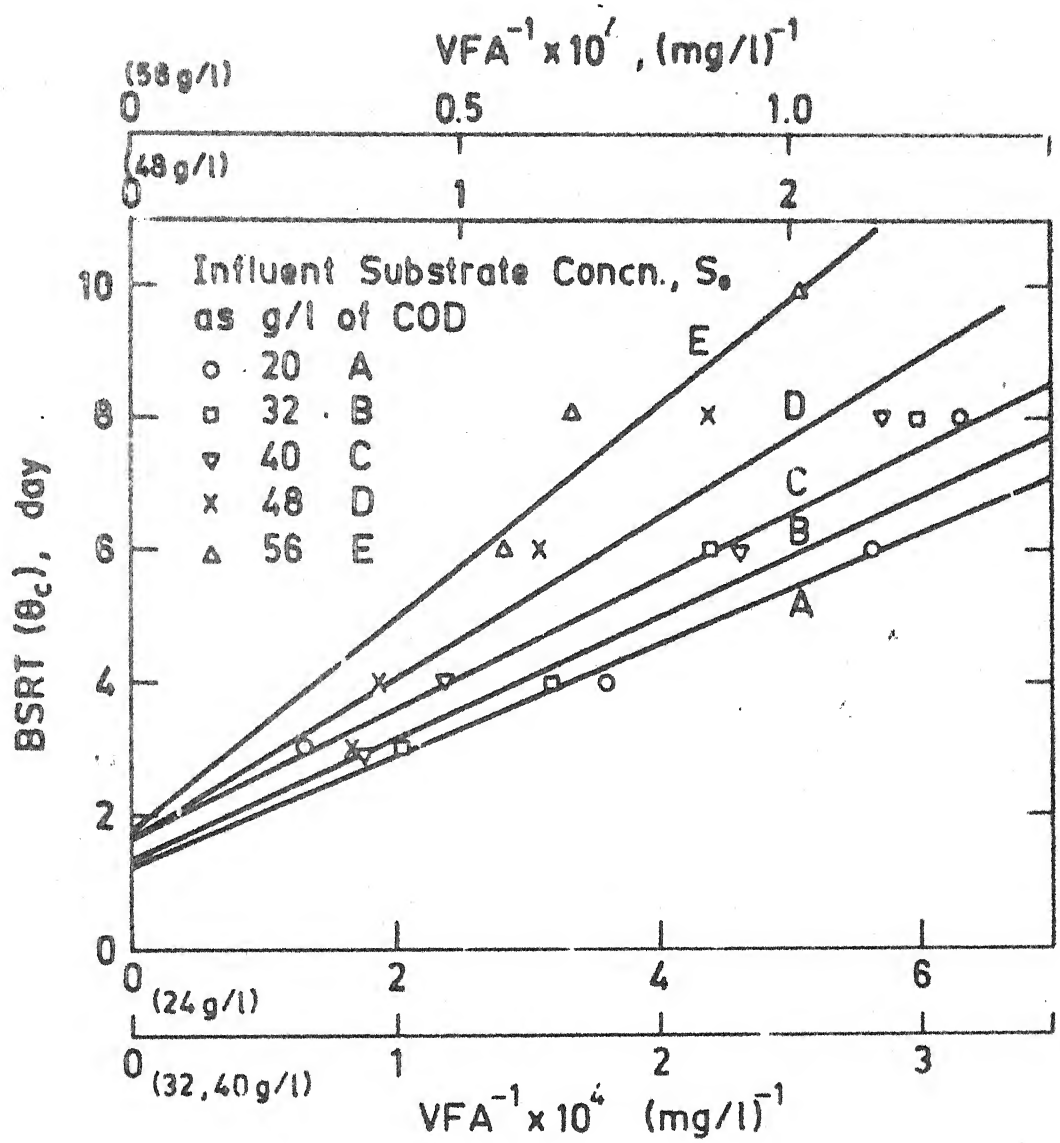


Fig. 5.1. Steady State Effluent VFA as Function of Biological Solids Retention Time (BSRT). Molasses as Substrate.

values. Now, a plot between q and $\mu=(1/\theta_c)$ was prepared to find out Y and K_d as per equation 2.6

$$\mu = Y q - K_d$$

These values have been presented in Table 5.1.

5.1.1.3. Biomass (M) Determination

Biomass concentration (M) for a particular S_o and θ_c combinations have been calculated using equation 2.7

$$\frac{1}{\theta_c} = \mu = Y \left(\frac{F}{M}\right) - K_d$$

where, F is organic loading in terms of Kg COD/m^3 day

M is biomass concentration expressed as Kg/m^3.

Using the constants Y and K_d which have already been evaluated from VFA data, and corresponding θ values the biomass concentrations for various substrate concentrations have been calculated and presented in Table 5.1.

5.1.1.4. B_o, μ_m and K_H Determination

The values of $_m$ and other constants were evaluated by the gas data as proposed by Chen and Hashimoto (1978). The quantity of methane produced was converted to that at NTP and was used to determine the methane yield (B) in ml CH_4/g COD added or destroyed and volumetric methane yield (G_s) in ml CH_4/l digester day. As per Chen and Hashimoto (1978), B_o, the ultimate methane yield was obtained by extrapolating a plot between B and $1/\theta$ to $1/\theta = 0$. This procedure is used to evaluate B_o values for different S_o and is presented in Figure 5.2.

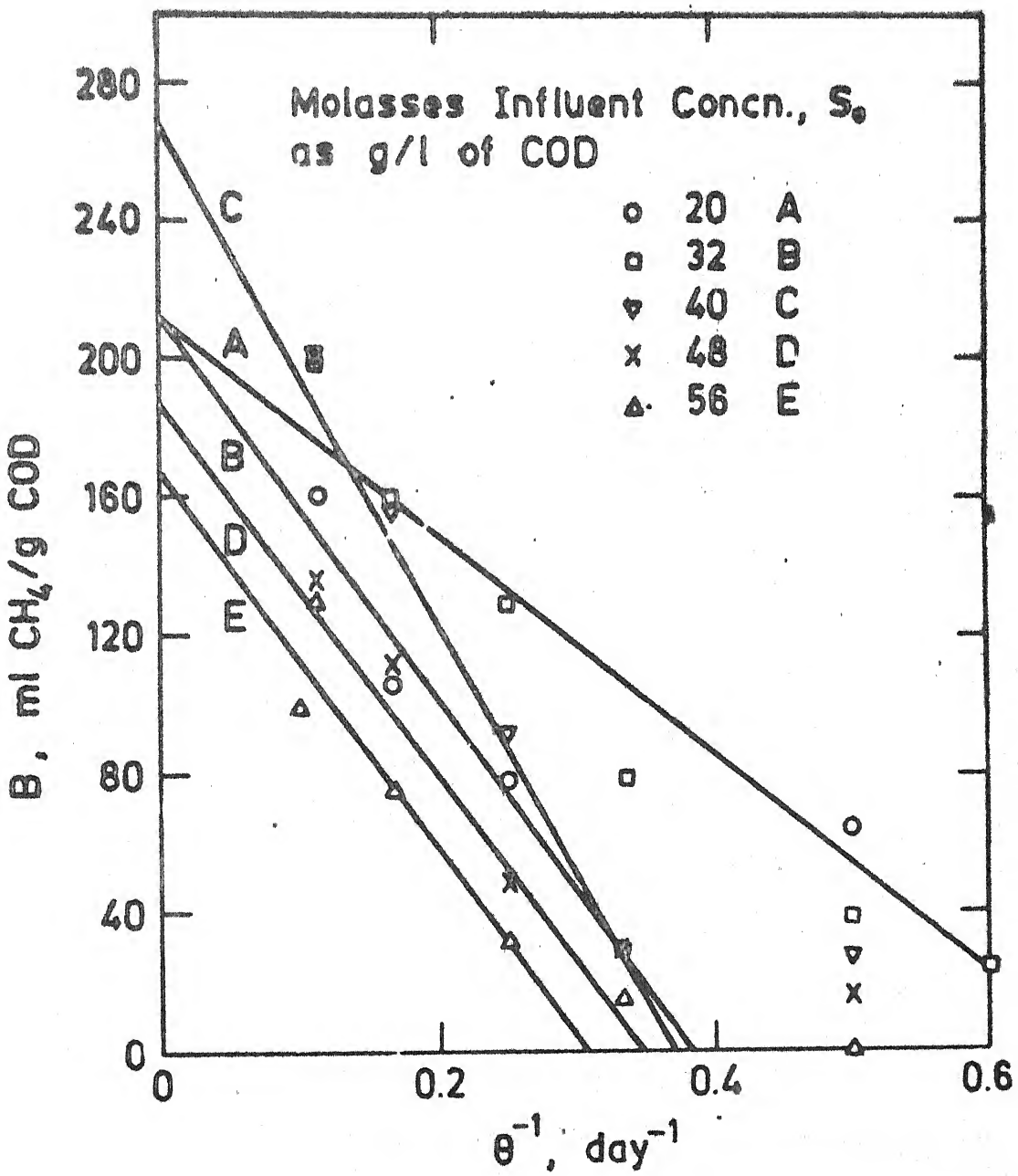


Fig. 5.2. Methane Yield (B) as a Function of Biological Retention Time (θ_c).

Rearranging the terms of equation 2.13 a linearized form is obtained which is as follows:

$$\frac{B_o}{B_o - B} = \frac{\mu_m}{K_H}\theta + \frac{K_H - 1}{K_H} \qquad 5.3$$

Using the computed values of B_o for a particular substrate and its concentration, $B_o/(B_o - B)$ was calculated for different value of B corresponding to different θ or θ_c. This was plotted against θ in Figure 5.3 which yields μ_m and K_H. Using equations 2.15 and 2.16, for different S_o, G_{max}, the maximum volumetric methane yield and θ_{Gmax}, the detention time was calculated. Besides, Figures 5.4a and b show the experimental volumetric yield (G_s) as a function of θ. It can be seen that as θ_c is reduced, the volumetric methane yield increased to a maximum and on further decrease in θ_c, resulted in decrease in gas yield, with subsequent failure of the system. The maximum gas yield (G_{max}) and the time at which this occurs (θ_{Gmax}) have been presented in Table 5.1 along with the computed values.

5.1.2. Comparison of the Kinetic Parameters

All the kinetic parameters evaluated for molasses at different influent substrate concentrations from different approaches are presented in Table 5.1 for comparison.

The result obtained using VFA data pertains to methanogens utilizing fatty acids for growth and that of evaluated as per Chen and Hashimoto (1978) indicates the combined activity of different species of methanogens producing

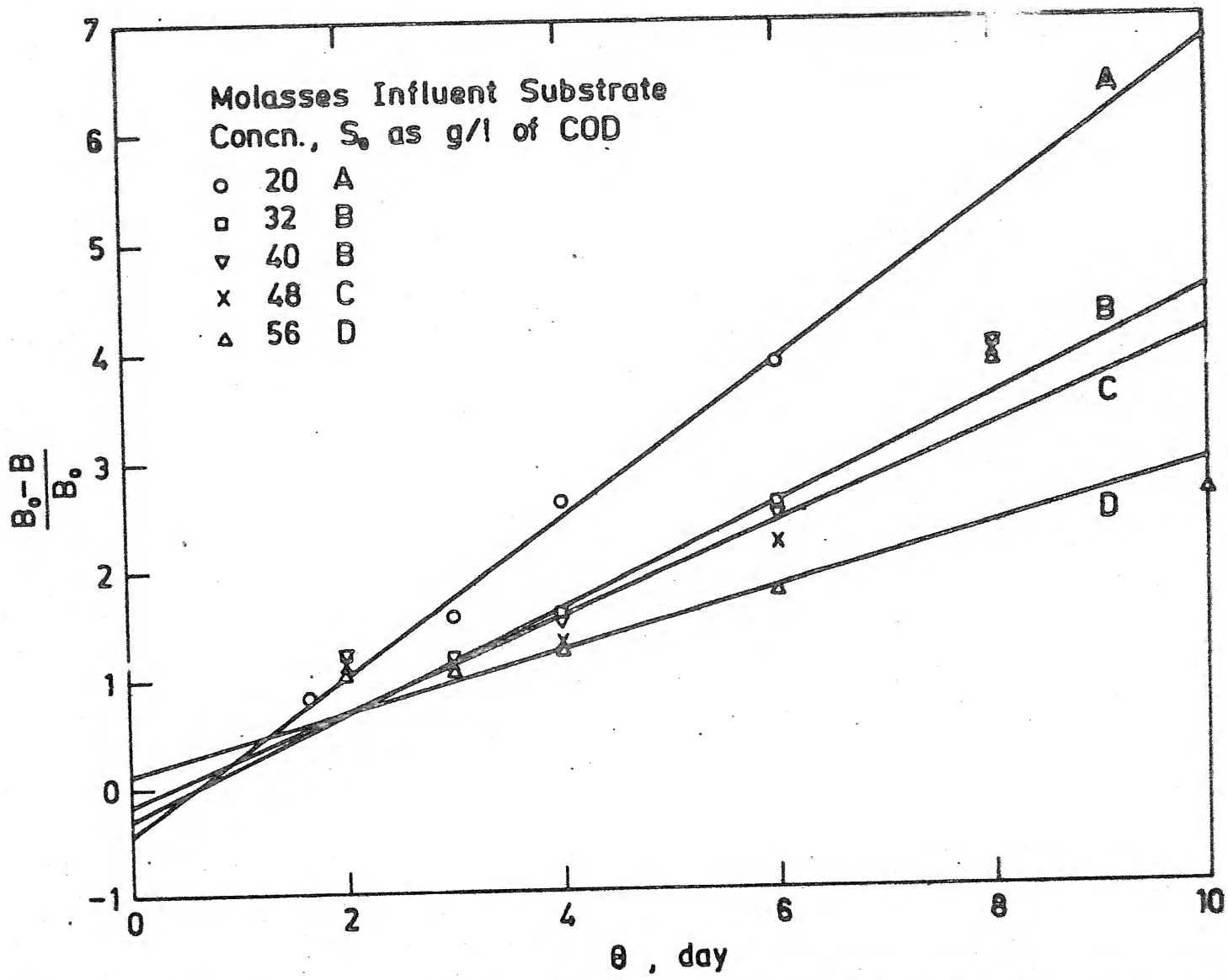


Fig. 5.3. Linearised Kinetic Model Relating Ultimate Methane Yield (B_o), Methane Yield (B) and BSRT (θ_c)

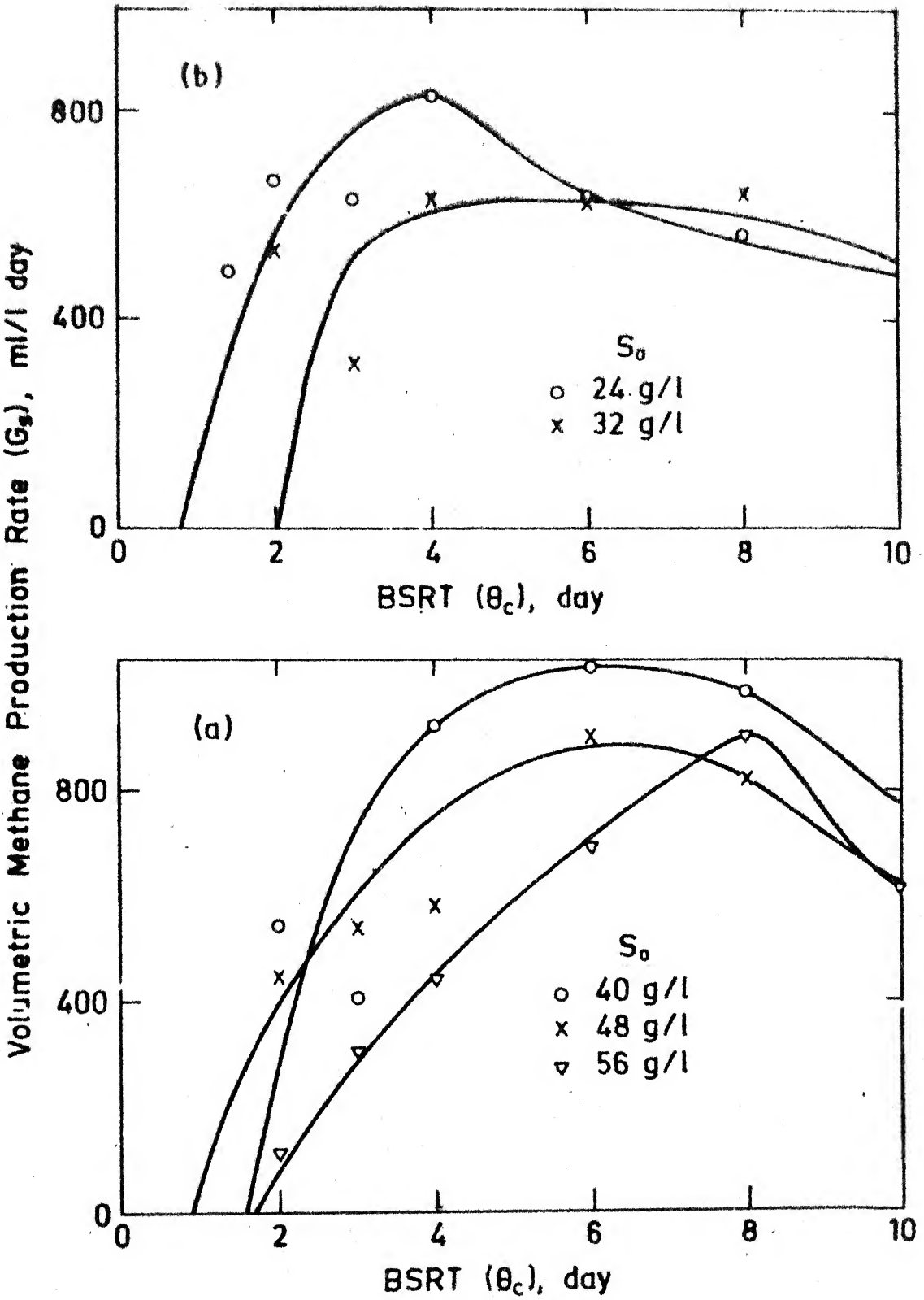


Fig. 5.4. Effect of BSRT (θ_c) on Volumetric Methane Production Rate (G_s) for Different Molasses Concn. (S_o).

Table 5.1. Evaluated Kinetic Parameters for the Anaerobic System Fed with Molasses

Influent load (S_o) mg/l as COD	From VFA data						From gas data							
	K_s, mg/l as CH_3COOH	μ_m day^{-1}	K_d day^{-1}	Y	Values calculated for θ_c = 8 days		B_o ml CH_4/g COD	μ_m day^{-1}	θ_m day	K_H	From calculation		From graph	
					θ_c day	Biomass (M) in mg/l					θ_{Gmax} day	G_{max} ml CH_4/l day	θ_{Gmax} day	G_{max} ml CH_4/l day
24	6080	0.76	0.05	0.096	6.34	1000	212	0.34	2.94	0.55	5.1	570	4	800
32	15770	0.83	0.05	0.096	6.83	1325	212	0.31	3.22	0.74	6.0	608	6	631
40	11170	0.59	0.07	0.065	7.10	1666	265	0.31	3.22	0.74	6.0	950	6	1000
48	18228	0.59	0.095	0.065	7.10	2000	181	0.33	3.03	0.66	5.5	902	6	840
56	45680	0.57	0.115	0.120	7.20	2325	181	0.29	3.45	1.33	7.4	655	8	700

methane from both the acetoclastic and hydrogen oxidising reactions.

As seen in the Table 5.1, the maximum growth rate constant (μ_m) for VFA data first increases from 0.76 to 0.83 (for S_o = 24 g/l and 32 g/l respectively) and then becomes almost constant at 0.59 (for S_o = 40 g/l and 48 g/l respectively) and then decreases to 0.57 (for S_o = 56 g/l). As μ_m should remain constant, the increase in μ_m value from 0.76 to 0.83 for molasses concentration of 24 and 32 g/l can be explained as the experimental error and hence an average value of 0.8 for μ_m can be adopted. However, the decrease in $_m$ value, later on, may indicate the inhibition of gas formers due to high VFA levels. The corresponding decrease in yield coefficients and increase in decay constants upto S_o = 48 g/l also substantiate the above fact. However, there is increase in both Y and K_d values for a feed concentration of 56 g/l. Nevertheless, the inhibition is not to a high extent and one may increase the substrate concentration as high as 48 g/l without loosing much in terms of growth rate. However, at higher load, the VFA level increases to a quite high level (as high as 23000 mg/l) and consequently there is a decrease in pH and hence to keep the digester alive at this high COD loading rate, care must be taken to maintain the pH around 7 by adding enough alkali which incurs additional cost.

While variations in μ_m for different substrate concentration is not much and can be assumed to be same, K_s values increase progressively (except for S_o = 40 g/l). This shows

that the maximum growth rate is reached at lower steady state VFA value for low influent substrate concentration, while the same is obtained at higher steady state VFA value for high influent substrate concentration. The figure presented in Figure 5.1 also indicates that the intercept on y-axis (μ_m) being almost same, the slopes (K_s/μ_m) of the lines significantly differ for different substrate concentrations.

The various parameters found by gas data as per Chen and Hashimoto (1978) have also been listed in the Table 5.1. The B_o values initially increase and then decrease which further shows that the influent load of 24 g/l may be limiting whereas substrate of influent load of 56 g/l is inhibitory. The value of K_H, however, increases (except for 48 g/l). Hashimoto (1982) has demonstrated that the K (same as K_H) values for different influent versus concentrations of cattle waste increase with the latter and a higher K value indicates growth inhibition due to overloading. The sharp increase in K_H value for the feed concentration of 56 g/l of molasses and decrease in μ_m tend to indicate the inhibition due to overloading.

Moreover, μ_m values for molasses concentration upto 48 g/l is almost same within the experimental error. Chen and Hashimoto (1979) employed the data of Varel *et al.* (1977) who had worked on beef waste taking influent versus concentrations of 59, 78, 97, 117 g/l and found μ_m values from gas data to be same, i.e., 0.77 day^{-1}. The VFA data of Varel *et al.* (1977) was employed by the present author to find μ_m. There was a great variation in μ_m values for

different substrate concentration. In fact the variation in μ_m values from VFA data in the present study is much less.

If μ_m from VFA and from methane data are to be compared, the data for different influent substrates in the latter case is more "stable". This is because of the fact that there is less possibility of making error in getting gas data compared to VFA data. In case of gas, there is a check whether the actual gas is coming or not, while in case of VFA calculation, its accuracy depends upon the number of stages and the correctness of procedure adopted.

The Table 5.1 also gives the biomass concentrations for different influent loads. As the influent substrate concentration increases, there is a proportional increase in the steady state biomass, as well. This further shows that the system can take up the higher loads without affecting the system much.

5.1.3. Performance of Digesters Under Least and the Most Stressed Conditions

The least and the most stressed conditions will occur at the higher and the lower BSRT, respectively for a given influent concentration. A plot of COD loading rate against VFA and methane production for the least and the most stressed conditions are presented in the Figures 5a and b respectively. For the least stressed condition, i.e., at θ = 8 days, the VFA level increases from 1590 mg/l to 14780 mg/l, however, methane production first increases upto COD loading rate of 5 Kg/m^3 day and then decreases sharply. The increase in methane production, in the beginning,

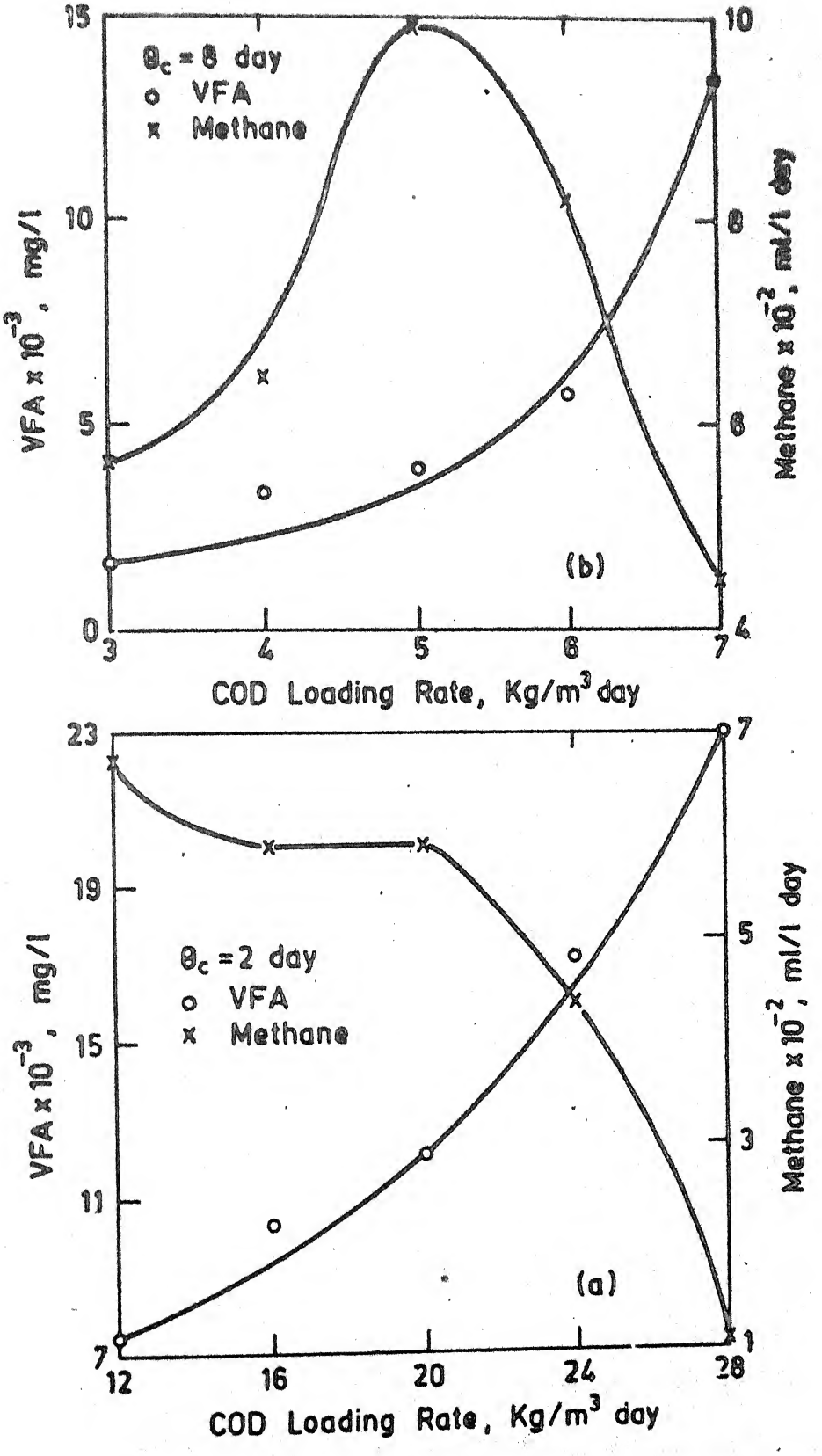


Fig. 5.5. Digester Performance w.r.t. Loading Rate

may be attributed to the fact that the initial increase in VFA helps to provide substrate to the methanogens while later, methanogens find themselves unable to compete with the rate of acetogens.

However, unlike the least stressed condition, the most stressed condition, i.e., at θ = 2 days, the VFA increases almost equally throughout with the COD load; methane production initially decreases slowly upto 20 Kg/m^3 day and then decrease is sharp. Hence, in this case, the loading rate for maximum production of methane would have been much earlier (perhaps, at 5 Kg/m^3 day of COD loading rate as evidenced in the least stressed condition).

5.1.4. Kinetics of Gas Production

The kinetics of total gas during 24 hours for molasses with substrate concentration of 24 g/l with θ = 2 and 8 days, after feeding was studied. Similar observations were made on the subsequent day after passing the gas through KOH trap to determine methane content. The results have been plotted in Figure 5.6. The total gas production is prelude of both acetogens and methanogens whereas methane production is because of the activity of methanogenes only. For a value of θ = 8 days, i.e., at COD loading of 3 Kg/m^3 day, the production of total gas and methane increase almost equally, unlike for θ = 2 days, i.e. at COD loading of 12 Kg/m^3 day. This may be due to the fact that at higher load, initial production of VFA is too high which becomes inhibitory to methanogens while this is not so in case of lower loads. However, the rate of methane production is slightly higher for high loading condition. This

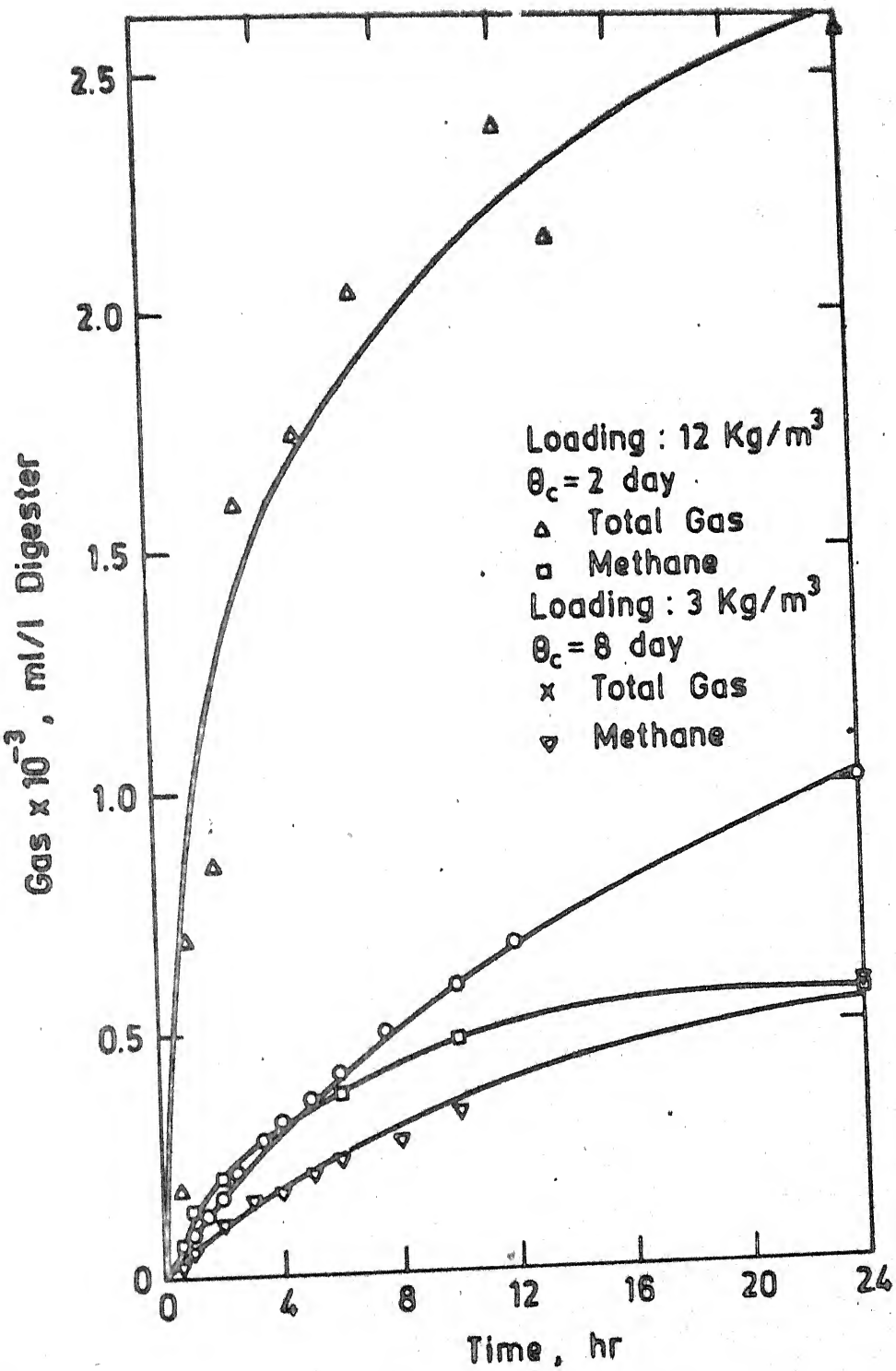


Fig. 5.6. Kinetics of Fermentation Process at Steady State. Molasses Concn. 24 g/l as COD.

shows that although total percentage of methane may be low for higher loadings, the total production of methane will be high for higher loadings.

Again the rate of production of gas is high in initial stage (in 8 hours) and then the rate decreases. This phenomenon is more predominant in case of methane production.

The percent extractable energy with respect to the theoretical energy, or the efficiency of the digester, has been calculated for influent loading rates. The theoretical methane production per Kg of COD destroyed under anaerobic condition is 0.35 m^3 at NTP (McCarty, 1964). The efficiency of the digester may be calculated as

$$\eta = \frac{m^3 \text{ of methane per Kg of COD destroyed}}{\text{Theoretical } m^3 \text{ of methane per Kg of COD destroyed}} \times 100$$

The efficiency in the least stressed condition represented by S_o = 24 g/l at θ = 8 days is 53.7% and that in the most stressed condition for same S_o at θ = 2 days, efficiency is 16.1%. The decrease is due to overloading. That is to say, the volume of methane that can be extracted per Kg of COD destroyed decreases as COD load increases. Further the load of 56 g/l with 2 days HRT which represents the most stressed condition in this investigation, the efficiency of extraction of energy is only 0.25%, i.e., most of gas produced is CO_2.

Thus, it appears to be appropriate to destroy COD to lesser extent in a roughing unit so as to produce maximum gas as per Figure 5.4 and remove the residual COD in

polishing units. The results on these aspects are presented in succeeding section.

5.2. Performance of Polishing Units Receiving Effluents from Roughing Units

5.2.1. Comparison of Different Digesters

As evidenced in Section 5.1, the production of methane per Kg is high at optimum detention time, however, it may not yield high COD removals. For higher COD removal, one has to have higher detention times but at this high detention time methane production per day will decrease as per Figure 5.4. In order to meet these two contrasting criteria together, first digester can be operated at low detention time for getting maximum gas production (known as roughing unit) and another receiving effluent from the first at high detention time to meet the COD removal criteria (known as polishing unit). However, an investigation is required to study the feasibility of treatment of the effluents from roughing unit in a polishing anaerobic unit. The effluent from first digester may contain many toxic materials which affect the microbes besides VFA.

For this study three such combinations have been employed. In the first combination, a glucose (12 g/l) digester was first brought steadily to θ=2.6 days to get maximum methane production. Then, the effluent from this digester was treated in five litre digesters with θ = 4, 6, 8, 10, and 16 days. Another roughing digester with glucose 20 g/l as feed was stabilized at θ = 2.6 days (i.e., it was not allowed to stabilize progressively and hence methane formers

were less) and was polished in six 1-litre digesters, to study the behaviour at high VFA levels. Yet another digester with molasses as influent load of S_o = 14 g/l with θ = 4 days was used for polishing its effluent in three 1-litre digesters at θ = 4, 8, and 12 days. A plot of θ against polishing unit VFA, percent COD removal, percent methane production, actual methane production and overall COD removal have been made for above combinations in Figures 5.7 to 5.9.

The Figure 5.7 of polishing digesters receiving effluents from glucose digester with S_o = 12 g/l and θ = 2.6 days (henceforth to be referred as $G_{12,2.6}$, for brevity) shows that percent COD removal increases rapidly upto θ = 8 days and then there is a very slow increase in it. Similar trend is shown in COD removal for the combination of roughing and polishing units (overall system). At θ = 8 days, 89% and 94% COD removal in polishing unit and overall system, respectively can be obtained, whereas the increase in COD removal is marginal when θ is doubled i.e. 16 days. It may be said that after certain detention time, COD removal is not very efficient. However, for the polishers receiving effluents from glucose digester with S_o = 20 g/l and θ = 2.6 days (henceforth, to be referred as $G_{20,2.6}$) which was deliberately stabilized at high VFA to study its effect, 80% and 89% COD removals were respectively, obtained at θ = 8 and 20 days (Figure 5.8). In case of the digesters receiving effluents from molasses digester with S_o = 14 g/l as COD and θ = 4 days (henceforth, to be referred as $M_{14,4}$), 65% COD removal is achieved at θ = 8 days, thereafter, there

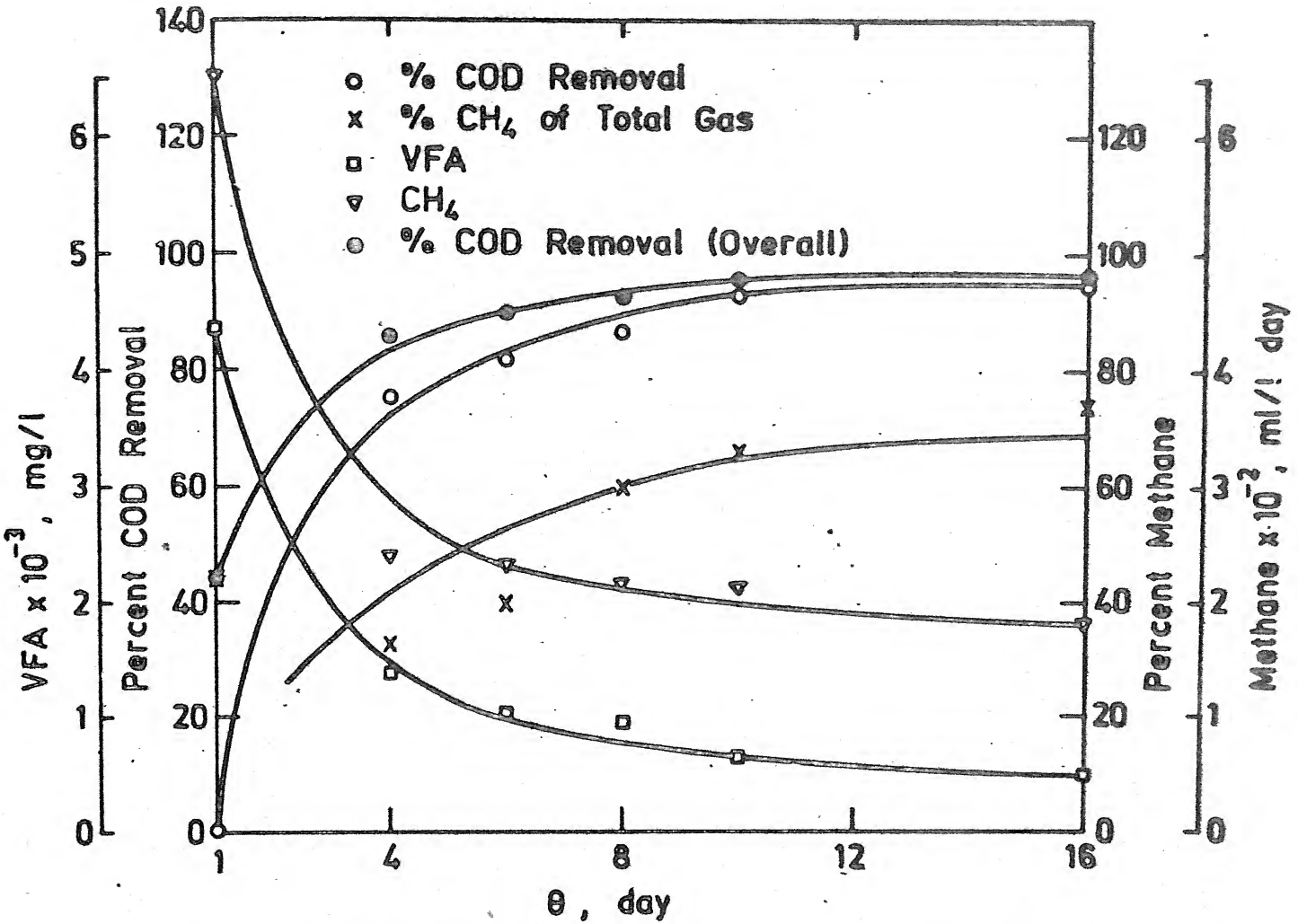


Fig. 5.7. Performance of Polishing Units for Receiving Effects from Roughing Glucose Digester (S_o=12 g/l as Glucose, θ=2.6 Days.

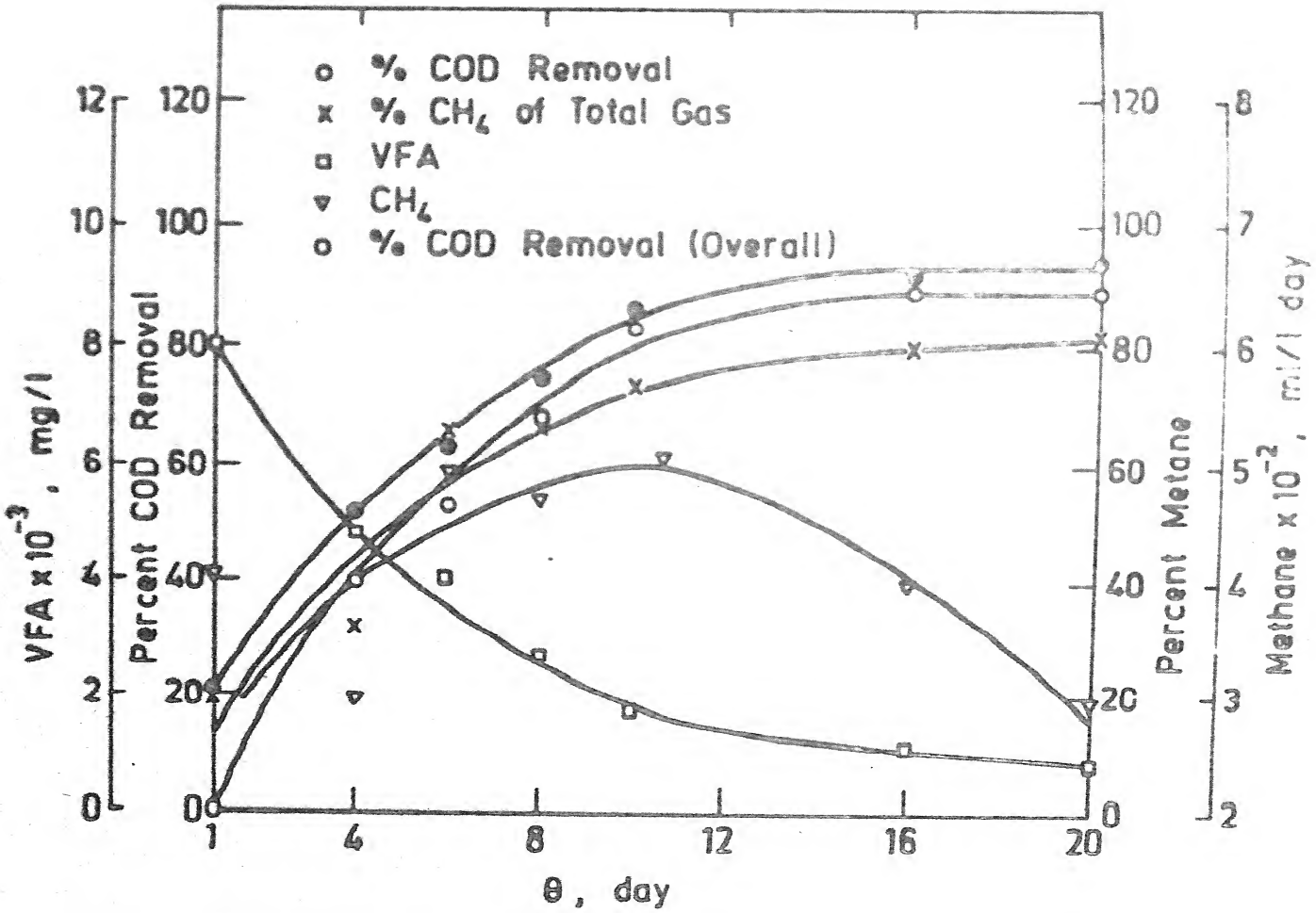


Fig. 5.8. Peformance of Polishing Units for Receiving Effluents from Roughing Glucose Digester (S_o = 20 g/l as Glucose, θ = 2.5 Days)

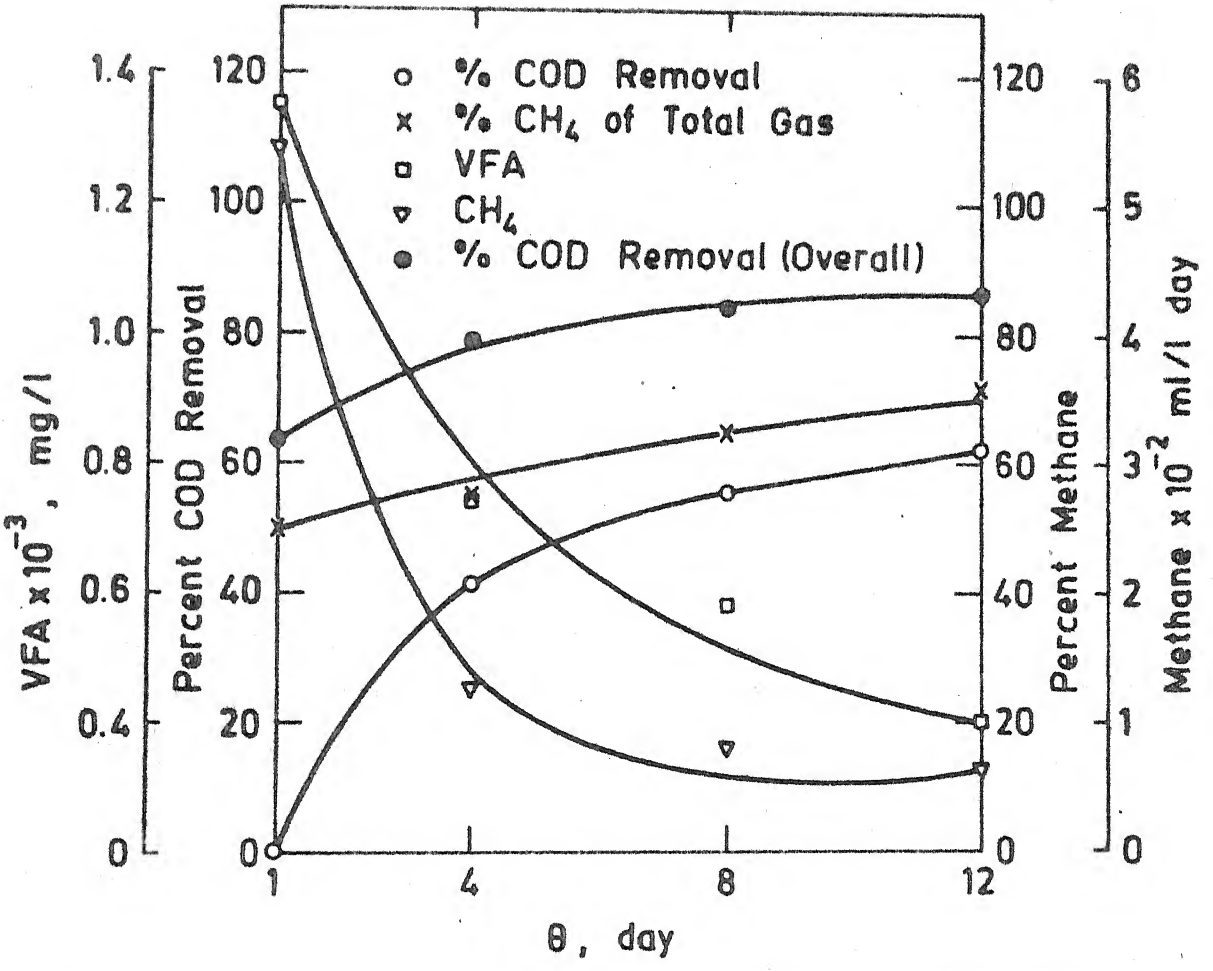


Fig. 5.9. Performance of Polishing Units for Receiving Effluents from Roughing Molasses Digester (S_o=14 g/l as COD, θ=4 days)

is negligible increase in removal (Figure 5.9). The higher detention times required for COD removed in case of $G_{20,2.6}$ polishing digester may be due to the fact that while in other roughing glucose digester ($G_{12,2.6}$), VFA levels have been brought down by progressively increasing the load and hence removing a major portion of COD in the roughing digester itself, the same is not the situation with $G_{20,2.6}$ digester which has high VFA levels. Besides, the latter roughing unit also received high influent substrate concentration.

In all three set of polishing digesters, as expected VFA level decreases and percent methane increases because of the fact that methanogens are finding enough chance to medicate. However, in case of $G_{20,2.6}$ polishing digesters, the methane production first increases upto θ = 10 days and then decreases, unlike other two combinations. This may be due to the fact that $G_{20,2.6}$ has a high VFA level and hence limiting substrate condition occurs later, unlike the other two sets where limiting substrate conditions are predominant from the beginning. Hickey and Owens (1981) worked on acid whey treating it by Anaerobic Biological Fluidized Beds in series. They found that overall COD removal in the series system is much higher than the system operating as one digester with combined substrate concentration and detention time. This investigation also provides an evidence that the effluent of the roughing unit can be treated anaerobically in polishing unit.

5.2.2. Kinetic Constants for Polishing Units

μ_m and K_s with respect to VFA and COD have been found out for all polishing combinations by the method described in Section 5.1.1.1. The values have been presented in Table 5.2.

Table 5.2. Evaluated Kinetic Constants for the Polishing Units

Designated digester	Influent COD (S_o) for polishing digester, mg/l	From VFA data		From COD data	
		μ_m day^{-1}	K_s mg/l as CH_3COOH	μ_m day^{-1}	K_s mg/l as CH_3COOH
$G_{12,2.6}$	6800	0.61	5083	0.61	5083
$G_{20,2.6}$	15777	0.83	7000	0.83	7000
$M_{14,4}$	5000	0.55	2200	0.55	2200

The kinetic constants for polishing units receiving effluents from roughing unit $G_{20,2.6}$ are lower than those of polishing units of $G_{12,2.6}$. Thus, there appears to be inhibition due to overloading of polishers of $G_{20,2.6}$. Grasius (1983) has reported them to be equal to 0.49 day^{-1} for single system of glucose digester receiving influent glucose concentration of 20 g/l. If two digesters in series are employed as in the present case, the extent of inhibition is less. The COD values are also providing the same kinetic constants. The polishing units treating effluent

of glucose. This shows that the tendency of wall growth in case of molasses is much higher than that of glucose.

A plot of COD loading rate vs. methane production and VFA has also been presented in Figure 5.11. As can be seen from this figure, the variation in VFA and methane production is very little in case of molasses. It shows that with every detention times, more microbial layer attaches to the wall and consequently they are able to take the increased load to produce almost the same VFA and methane but increased percentage of CO_2. The COD removal is expected to be more because its higher content in the off gas. However, in case of glucose, this behaviour is not shown. Here, methane production increases initially and then decreases, VFA level also shoots up at COD loading rate of 20 Kg/m^3 day. Jain (1984) reports that μ_m remains constant whether the microbes are growing in suspended system or attached one, on the surface like cinder, coal etc. Assuming μ_m to be same for the wall growth of microbes as that in the system without wall growth for a given substrate, and utilising corresponding steady state VFA for wall growth systems, it is possible to calculate the BSRT. The μ_m values for suspended growth reacters for molasses (Table 5.1) and for glucose (Iyengar, 1984) have been adopted.

In order to study the behaviour in sudden loading on the wall growth — a glucose digester having S_o = 8 g/l as glucose and θ = 8 days (COD loading rate = 1 Kg/m^3 day) was implied and subsequently loaded with an influent glucose concentration of 20 g/l (COD loading = 20 Kg/m^3/day). It

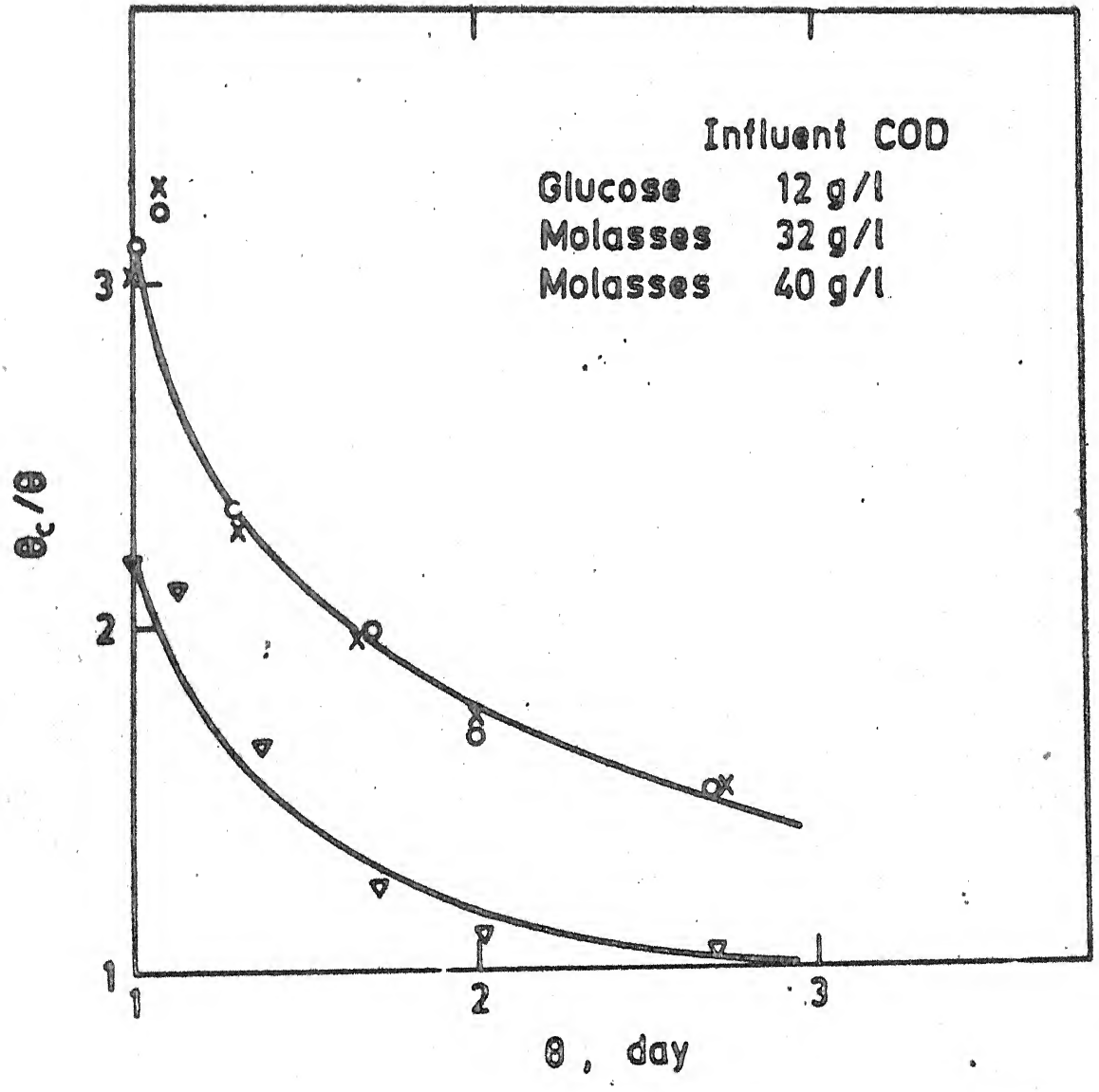


Fig. 5.10. Effect of HRT (θ) on BSRT (θ_c) for Digesters with Wall Growth.

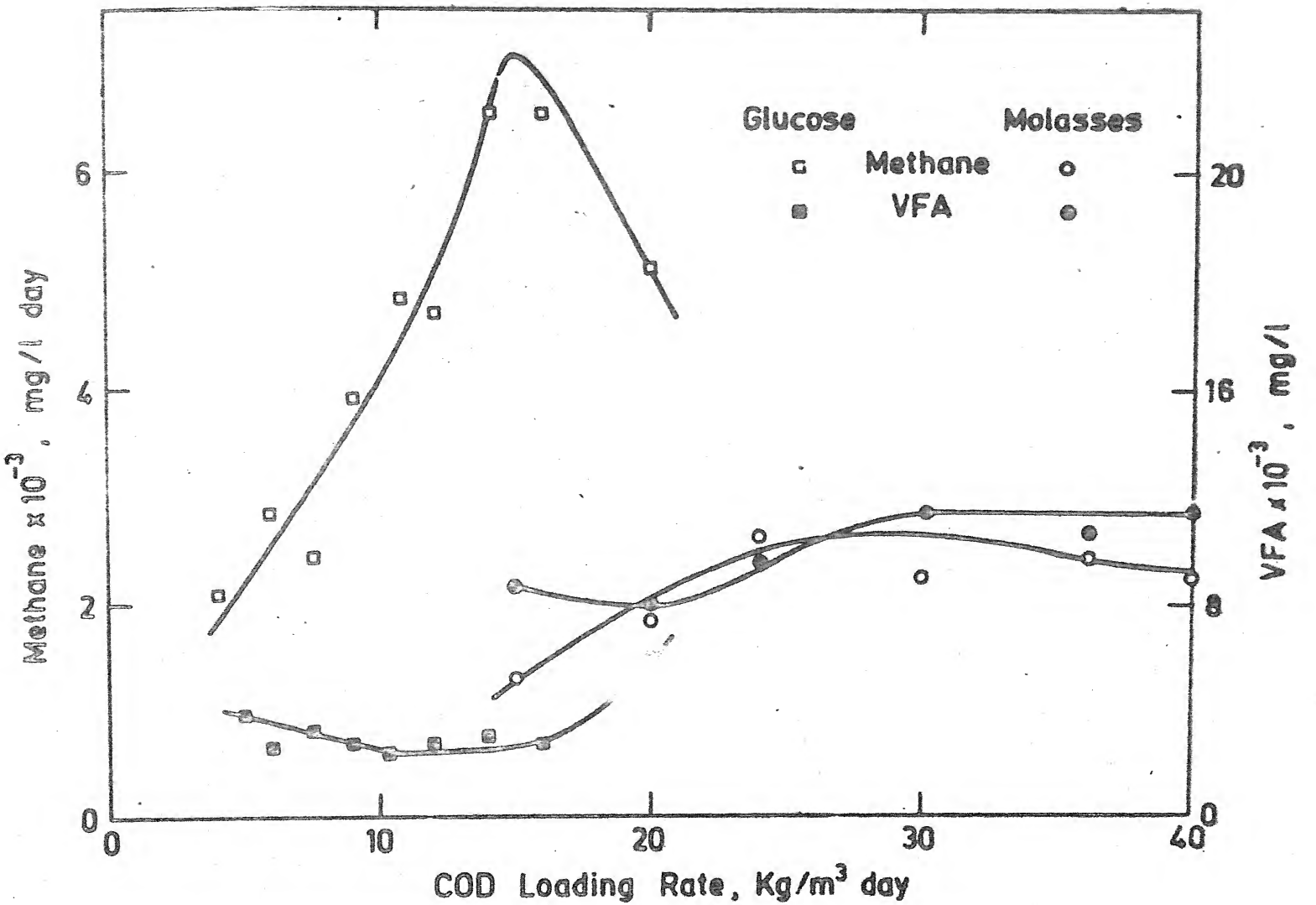


Fig. 5.11. Performance of Digesters with Wall Growth.

from roughing unit $M_{14,4}$ gave a μ_m value of 0.55 day^{-1}. In the present study an average of μ_m of 0.8 day^{-1} was obtained in a single system of digesters receiving COD upto 32 g/l. The decrease in this value for the polishers receiving the complex effluent from molasses digesters may be due to the presence of toxic materials in it. This indicates inhibition occurring in polishers.

5.3. The Effect of Wall Growth on the Performance of the Digester

It was seen that with time, microbial mass deposits on the inner walls of the digester. This phenomenon is more predominant at lower detention times when loading rates are high. Also, in case of molasses, this phenomenon is more appreciable than glucose because of stickiness of molasses. This wall growth also contributes in terms of methane production and hence it was felt to study its behaviour systematically.

5.3.1. Calculation of BSRT (θ_c)

Since a part of microbial mass is attached to the wall of the digester, hence in this case HRT(θ) and BSRT (θ_c) are not the same. Equation (2.1) gives a relation between BSRT and μ_m and steady state substrate concentration as

$$\frac{1}{\theta_c} = \frac{\mu_m S}{K_s + S}$$

A plot of $\frac{\theta_c}{\theta}$ vs. θ have been presented in Figure 5.10 for both molasses and glucose as substrate. It can be seen that for molasses θ_c/θ variation against θ is more than that

was found that the VFA level increased from 350 mg/l to 7215 mg/l, total gas from 1400 ml to 17000 ml and percent methane decreased from 48.6% to 8.8% and there was a drastic decrease in pH. Hence, it may be concluded that to achieve the benefits of wall growth, it should be progressively loaded so as to allow enough time to methanogens to proliferate on the walls.

5.4. Treatability of Distillery Waste by Anaerobic Digestion

As actual wastes from distillery could be procured only during the later part of the investigation, preliminary studies regarding its treatability by anaerobic digestion were conducted.

Three digesters having 20 g/l COD and detention time equal to 8 days with three combinations were studied: (i) bicarbonate addition to raise pH and subsequent digestion with addition of nutrients, (ii) bicarbonate addition to raise pH and subsequent digestion in the absence of nutrients, and (iii) lime addition to raise pH and suplementationwi nutrient. The results regarding steady state VFA, methane content and percentage have been presented in Table 5.3.

Comparing the performance of digestion in first and second case as per Table 5.3, it was found that the steady state VFA and COD values are slightly higher and methane production and percent methane were slightly lower in the former. This shows that distillery waste contain most of the required nutrients in itself and supplementation of further nutrients does not provide any additional advantage.

Table 5.3. Treatability Study of Distillery Waste with S_o = 20 g/l as COD, θ = 8 days

S. No.	Type of digester		VFA mg/l as CH_3COOH	Methane ml/l at NTP	% Methane
	Addition of type of chemical for raising initial pH	Nutrient supplementation			
1.	Sodium bicarbonate	Nutrients added as per Table 4.1	12800	250	53
2.	Sodium bicarbonate	No addition of nutrients	11835	270	57
3.	Lime	Nutrients added as per Table 4.1	16125	75	51

The VFA and the effluent COD values for lime treated waste was much higher and methane production and percent methane were lower compared to other digesters. Further investigations are required in this regard.

6. SUMMARY AND CONCLUSIONS

The entire study was broadly divided into four parts. The first part deals with the effect of substrate (as molasses) overloading on the performance of the digester. The kinetic parameters for the process design was also evaluated. The kinetic constants for methanogens can be evaluated by VFA and gas data. The μ_m values with respect to VFA remains constant upto 48 g/l of load and then decreases for 56 g/l indicating the starting of inhibition. μ_m values computed from gas data as suggested by Chen and Hashimoto (1978) is fairly constant upto 48 g/l and then there is slight decrease for 56 g/l. This also shows that inhibition starts occurring at 56 g/l of influent COD load. The data with respect to gas is more consistent than that with respect to VFA — this may be due to the fact that measurement of gas does not involve any experimental error unlike VFA. Considering all these aspects, it was seen that 40 g/l of COD load for molasses is optimum for gas production and maximum growth. The percent extractable energy with respect to theoretical energy was calculated for different substrate concentrations and detention times. It was found that for lower load, it is high and is low for higher loads. The gas data were also used as suggested by Chen and Hashimoto (1978) to determine the maximum gas production and detention time at which the digesters are to be operated to achieve this.

The maximum gas production was achieved at some optimum HRT, however, COD removal is not to the required extent. In order to meet these two requirements simultaneously, two digesters — one roughing unit meant for maximizing methane gas and subsequent polishing unit receiving the effluent from the former has the task of maximum COD removal. It was seen that about 90% of COD removal is achieved for HRT of 8 to 10 days in polishing units. By further increasing HRT, there is very marginal increase in COD removal.

The performance of digesters having wall growth was also studied. It was found that the wall growth contributed significantly in terms of methane production and the BSRT increases as high as three times that of HRT. The wall growth appears to behave like a fixed film reactor.

Distillery waste does not need supplementation of nutrient for digestion besides initial pH adjustment of wastewater. The performance of the digester receiving lime treated effluent to adjust the pH is inferior to that treated with bicarbonate.

7. ENGINEERING SIGNIFICANCE

A particular industry over a period of time would like to expand or with increase in population the effluents to be treated will increase and going for altogether new digesters may prove to be uneconomical. Also it may not be possible to construct a new digester for slight or unrestricted increase in flow. This study provides an answer to that. One may overload the digesters to certain extent without much affecting its efficiency. Hence, until the effluents increase to a level as to call for new digesters, the existing one itself can be used. The major advantage of anaerobic digesters is that it provides energy apart from reducing the pollutional load. In order to achieve these to a maximum extent — a roughing unit for maximum gas production and an anaerobic lagoon for maximum COD removal can be used. This will reduce the cost of industry in constructing huge air-tight anaerobic digesters. For those industries which go for rapid expansion — the existing one may become roughing digester and only lagoon is to be constructed, hence reducing the cost. Also, over a period of time, thick microbial coating takes place on the wall of the digesters which contributes in increasing efficiency of the digesters. This reduces the volume of the digester and hence the capital cost. The inner walls of the digesters can be made rough so that the microbes attached to the walls can firmly be positioned.

8. SUGGESTION FOR FUTURE INVESTIGATION

Based on the present work, the following suggestions for the future investigations may be made:

1. Extensive experimentations with distillery wastes should be undertaken as it is the actual waste. Various kinetic constants viz., μ_m, K_s, Y, K_d and K_H should be evaluated for better understanding of the microbe's behaviour.
2. Studies should be conducted on the performance of anaerobic digestion using cheaper chemical like lime instead of bicarbonate to maintain digester pH.
3. For same substrate concentration and detention time, study should be conducted in reacters of different capacity and a factor of the size of the reacter can be calculated, so that the experimental results can be applied in the field.
4. Studies may be undertaken on number of digesters, more than two, in series. A comparison, in terms of COD removal, should be made with these digesters in series with different numbers.
5. A plug flow type of situation may be created to study anaerobic digestion on this aspect.
6. Different locally available low cost materials with various sizes and porosity should be used for surface and a study on it should be carried on.

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APPENDIX I

STEADY STATE EFFLUENT DATA

Steady state effluent data obtained in the study of "Effect of substrate (molasses) overloadings on the performances of the digester". S_o combinations = 24, 32, 40, 48 and 50 g/l as COD, BSRT (θ_c) combinations = 10, 8, 6, 4, 3, 2 and 1.67 days.

Abbreviations used:

S_o = influent substrate concentration in mg/l

C = COD load in kg/m^3 day

V = VFA is mg/l as CH_4COOH

G = G_s = ml CH_4/l day at NTP

B = ml CH_4/g COD added

% = percent methane present in the total gas

$$= \frac{m^3 \text{ of methane per kg of COD destroyed}}{\text{Theoretical } m^3 \text{ of methane per kg of COD destroyed}} \times 100$$

θ days		S_0 = 24 g/l	S_0 = 32 g/l	S_0 = 40 g/l	S_0 = 48 g/l	S_0 = 56 g/
10	C V G B %					5.6 9870 610 109 37.6 31.1
8	C V G B %	3 1590 564 188 56.4 53.7	4 3350 644 161 51 46	5 3500 991 198 69 56.6	6 5700 822 137 50.5 39.1	7 14780 903 129 48 46.9
6	C V G B %	4 1775 640 160 52.5 45.7	5.33 4500 622 117 46 33.4	6.67 4350 1036 155 52 44.3	8 8100 904 113 39.5 32.3	9.3 17583 698 75 16.4 21.4
4	C V G B %	6 2775 834 139 46 39.7	8 6300 631 79 30 22.6	10 8550 924 92.4 31.5 26.4	12 13172 588 49 22 14	14 16061 441 31.5 14.1 9.0

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θ days		S_0 = 24 g/l	S_0 = 32 g/l	S_0 = 40 g/l	S_0 = 48 g/l	S_0 = 56 g
3	C	8	10.67	13.33	16	18.7
	V	7690	9640	11340	15000	18400
	G	632	315	405	544	302
	B	79	30	30.4	34	16.1
	%	35	16	15	16.5	7
		22.6	8.6	8.7	9.7	4.6
2	C	12	16	20	24	28
	V	7500	10430	12130	17202	23000
	G	674	541	541	522	112
	B	56.3	39	27.1	18.4	4
	%	20	18	17	9.5	2
		16.1	11.1	7.7	5.3	0.25
1	C	15				
	V	6072				
	G	518				
	B	34.8				
	%	16.7				
		9.9				

APPENDIX II

Steady state effluent data for roughing and polishing units, roughing unit receiving glucose = 12 g/l as glucose and at BSRT (θ) = 2.67 days brought steadily from higher BSRT

Parameters	Roughing unit	Polishing units, BSRT (θ), days				
		4	6	8	10	16
COD, mg/l	6800	1700	1244	890	520	402
VFA, mg/l	4350	1380	1085	905	660	525
% CH_4	44.2	32.3	40	59	67	77
ml of CH_4/l day at NTP	658	239	234	216	216	180
% COD removal	0	75	81.7	86.9	92.4	94.1
Overall COD removal (%)	43.3	85.9	89.6	92.6	95.7	96.7

APPENDIX III

Steady state effluent data for roughing and polishing units, roughing unit receiving glucose = 20 g/l as glucose, stabilized at high VFA at θ = 2.67 days.

Parameters	Roughing unit	Polishing units, BSRT (θ), days					
		4	6	8	10	16	20
COD, mg/l	15777	9482	7360	5020	2720	1673	1262
VFA, mg/l	8000	4800	4000	2700	1700	1140	850
ml of CH_4/l day at NTP	405	288	496	469	505	396	297
% CH_4	20.1	32	66.3	66.7	73.7	79.3	82.5
% COD removal	0	40	50	66.4	78.8	85.8	89.4
% overall COD removal	21	52.6	63.2	75	86.4	92	94

APPENDIX IV

Steady state effluent data for roughing and polishing units, roughing unit receiving molasses = 14 g/l as COD at BSRT (θ) = 4 days

Parameters	Roughing unit	Polishing units, BSRT (θ), days		
		4	8	12
COD, mg/l	5000	2950	2230	1900
VFA, mg/l	1275	750	390	200
ml of CH_4/l day at NTP	541	126	81	68
% CH_4	50	56	64	72
% COD removal	0	41	55.4	62
% overall COD removal	64	79	84	86.4

APPENDIX V

Steady state effluent data for wall growth digesters (Abbreviations used as in Appendix I and M for methane/2 l of digesters.

θ		Glucose S_0 = 12 g/l	Molasses S_0 = 32 g/l	Molasses S_0 = 40 g/l
2.67	C	4.5	12	15
	V	3900	6938	8694
	M	2100	2090	1330
	%	56.8	27.8	16.6
	θ_c/θ	1	1.48	1.43
2	C	6	16	20
	V	2730	9000	8000
	M	2800	1795	1860
	%	51.9	22.4	18.6
	θ_c/θ	1.09	1.66	1.77
1.67	C	7.5	19.2	24
	V	3330	9200	9400
	M	2400	1840	2060
	%	37.5	24	23
	θ_c/θ	1.22	1.96	1.95
1.33	C	9	24.1	30
	V	2700	9900	13800
	M	3900	1800	2250
	%	42.5	26	27
	θ_c/θ	1.65	2.35	2.26
1.11	C	10.8	28.8	36
	V	2430	8100	9450
	M	4800	1950	2400
	%	44	27	29
	θ_c/θ	2.1	3.2	2.93
1	C	12	32	40
	V	2700	10000	11250
	M	4700	2250	2250
	%	35.5	24	22
	θ_c/θ	2.17	3.1	3